



Digitized by the Internet Archive
in 2008 with funding from
Microsoft Corporation

Chem. & Phys
C

THE

54

T

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

WILLIAM FRANCIS, PH.D., F.L.S.,

MEMBER OF THE CHEMICAL SOCIETY OF LONDON.

VOLUME IV. 1846.

360338
24. 1. 39.

LONDON:

PUBLISHED BY RICHARD AND JOHN E. TAYLOR,

RED LION COURT, FLEET STREET.

QUEEN'S COLLEGE

UNIVERSITY OF TORONTO



PRINTED BY RICHARD AND JOHN E. TAYLOR,
RED LION COURT, FLEET STREET.

THE CHEMICAL GAZETTE.

No. LXXVII.—January 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Alloxan, Alloxanic Acid, and some new Products of Decomposition of Uric Acid. By ADOLPH SCHLIEPER.

THE author, after passing in review the method described by Liebig and Wöhler, and that recently recommended by Prof. Gregory for the preparation of alloxan by the oxidation of uric acid by means of nitric acid, advises that nitric acid of 1.4–1.42 spec. grav. be employed instead of an acid of 1.3–1.34 spec. grav., as proposed by the latter chemist*.

He finds however the following to be the most advantageous method of preparing alloxan:—4 oz. of uric acid are mixed in an evaporating dish with 8 oz. of moderately strong muriatic acid. An ounce of finely powdered chlorate of potash is then gradually and slowly added. The mixture becomes warm, no gas is evolved, and the uric acid is completely decomposed into alloxan and urea—a further proof, if any were needed, that uric acid consists of urilic acid and urea. No chlorine is evolved if the process be properly managed, conducted slowly, and the mixture be well-agitated after each addition. When three-fourths or four-fifths of the chlorate have been added, the warm and fluid mass is diluted with 2 volumes of water. The mixture is set aside, the solution poured off, the remaining undissolved uric acid is treated with a little strong muriatic acid; and after the mixture has been heated to 122° F., the remainder of the chlorate is slowly added until the uric acid has dissolved. More than 1 oz. of the chlorate is never required for 4 oz. of the uric acid.

The solution of alloxan is now decomposed by sulphuretted hydrogen in the ordinary way to form alloxantine; the liquid filtered from this may be very advantageously employed to yield large quantities of nitrate of urea, by removing the excess of muriatic acid with oxide of lead, and treating the filtered liquid with excess of nitric acid. The impure alloxantine is separated from sulphur by

* See Dr. Gregory's observations on this subject at page 23.
Chem. Gaz. 1846.

recrystallization. It may then be very easily and perfectly converted into alloxan by nitric acid. Half the quantity to be used for this purpose is heated to ebullition in a flask with a double volume of water, and then nitric acid dropped into it; at first no action ensues, but as soon as the escape of nitrous oxide is perceptible no more is added, the flask is immersed in a bath of boiling water, the decomposition then proceeds regularly; as soon as the alloxantine has nearly disappeared, a further quantity is added; if the action ceases, a few drops more of acid cause its renewal. Care must be taken that at the end of the operation a little excess of alloxantine is present; the solution, filtered whilst hot, is treated with 3 or 4 drops of nitric acid, to decompose the alloxantine contained in it; it is then allowed to cool, when an abundance of crystals of alloxan are obtained.

Alloxanic Acid.—This may be readily obtained by decomposing alloxanate of baryta with dilute sulphuric acid, leaving the salt in slight excess. The author considers this acid as bibasic, and doubles the formula given by Liebig and Wöhler, making it in the hydrated state $C^8 N^2 H^2 O^8 + 2HO$; the water may be either perfectly or partially replaced by bases.

Neutral Alloxanate of Potash.—This salt is best prepared by mixing a concentrated solution of alloxan with an equal volume of concentrated solution of potash; strong alcohol is then cautiously added until the precipitate ceases to be redissolved; the solution is then rendered clear by the addition of a few drops of water. The salt crystallizes on evaporation in beautiful transparent and hard crystals. The crystallization is complete in about 48 hours, and may be renewed by the addition of more alcohol. If too much alkali be present, only a concentrated solution is at first separated by the alcohol; this however soon crystallizes. If too little potash be present, an acid potash salt is precipitated, which cannot be converted into the neutral salt by the addition of more alkali, on account of its insolubility in alcohol. The crystals are oblique rhomboidal prisms. It is readily soluble in water, not so in alcohol or æther, is bitter and neutral. It loses 5 atoms of water at 212° ; the 6th atom is not evolved even at a temperature of 302° , although the salt has commenced to turn yellow. It yielded on analysis—

	Found.			Equiv.	Calc.	
	I.	II.	III.			
Potash	32.03	31.98	..	2 =	1179.8	32.42
Carbon	..	..	16.48	8	600.0	16.51
Nitrogen ..	..	..	..	2	354.0	9.74
Hydrogen. . .	..	..	2.86	8	100.0	2.75
Oxygen ..	..	..	..	14	1400.0	38.58
					3633.8	

The salt, dried at 212° , is composed of $C^8 N^2 H^2 O^8 + 2KO + HO$. Dried in the air it consists of $C^8 N^2 H^2 O^8$, $2KO + 6aq$.

Binalloxanate of Potash.—This salt is prepared from alloxan in the same manner as the last, except that excess of alloxan is used

instead of excess of potash. 2 or 3 parts of solution of alloxan are mixed with 1 of potash; excess of alcohol is then added; the salt falls as a crystalline granular powder. It is rather insoluble in water and alcohol, but more soluble than the neutral salt. It has an acid reaction, and becomes red on exposure to the air. When dried at 212° , it consists of $C^8 N^2 H^2 O^8$, $KO + HO$, yielding—

		Calculated.	I.	II.
1 atom Potash	589.9	23.77	23.32	23.41
1 atom Alloxanic acid	1779.0	71.69		
1 atom Water	112.5	4.54		

Neutral Alloxanate of Ammonia.—This compound rapidly evolves ammonia, and is converted into the acid salt. It is obtained by treating a solution of the acid salt in ammonia with excess of strong alcohol. It forms a white crystalline mass, which is washed with æther, pressed between blotting-paper, and dried over lime. The proportion of nitrogen to carbonic acid was as 1 to 2.37. The proportion in the neutral salt should be 1 : 2, in the acid salt 1 : 2.66; hence it was merely a mixture of the two.

Binalloxanate of Ammonia.—This is readily obtained by saturating alloxanic acid with ammonia; the solution, exposed to a gentle heat, crystallizes. When it is attempted to form this salt like the potash salt from alloxan, mycomelanate of ammonia only is obtained. It forms hard, transparent, yellowish crystals. It is soluble in 3 or 4 parts of water, not in alcohol. On destructive distillation it yielded ammonia, carbonic, cyanic and hydrocyanic acids, oxamide and urea.

When burnt with oxide of copper, the nitrogen and carbonic acid evolved were in the relation of 3 : 8. Dried at 212° , it yielded—

	Found.		Atoms.	Calc.
	I.	II.		
Carbon	26.74	26.75	8	27.04
Nitrogen	23.66	23.67	3	23.93
Hydrogen	4.40	4.09	7	3.93
Oxygen	45.30	45.49	10	45.10

leading to the formula $C^8 N^2 H^2 O^8 + NH^4 O + HO$.

Neutral Alloxanate of Baryta.—This is best obtained in quantity by mixing a cold saturated solution of alloxan with a cold saturated solution of chloride of barium, in the proportion of 2 volumes of the former to 3 of the latter. The mixture is heated to 140° – 158° , and solution of potash gradually added, the whole being constantly agitated; on each addition of the potash a caseous white precipitate is formed; this re-dissolves on agitation; the addition of the potash is continued until the white precipitate ceases to be re-dissolved; a heavy granular crystalline powder of alloxanate of baryta is almost immediately formed, and rapidly subsides, which is then washed. It consists of $C^8 N^2 H^2 O^8$, $2BaO + 4aq$.

Binalloxanate of Baryta.—This is always formed in preparing alloxanic acid from the neutral barytic salt by means of sulphuric acid; if an insufficient quantity of the acid has been added to de-

compose the salt, we obtain a solution of alloxanic acid mixed with this salt; the latter separates from it in crystalline crusts when kept for some days in a cool place; it forms small white opaque warts. It is also readily obtained by mixing a solution of binalloxanate of ammonia with one of chloride of barium, and setting the mixture aside for several days.

It is acid, much more soluble in water than the neutral salt, also soluble in alcohol. When dried in the air it yielded—

	I.	II.	III.	IV.	Atoms.	Calc.
Carbon	..	..	..	19.15	8	19.52
Nitrogen ..	..	..	..	..	2	11.40
Hydrogen ..	..	..	..	2.22	5	2.22
Oxygen	..	..	..	..	11	35.73
Baryta	31.58	31.91	31.99	..	1	31.13

Basic Alloxanate of Baryta.—This is prepared by treating a solution of alloxan and chloride of barium with ammonia; it forms a gelatinous precipitate. It may also be obtained when a solution of alloxan is treated with an excess of barytic water. It is soluble in a large quantity of water and in acids, has a strongly alkaline reaction, and readily absorbs carbonic acid from the air.

Neutral Alloxanate of Lime.—This was obtained by treating a concentrated solution of neutral alloxanate of potash with one of chloride of calcium. It forms small shining crystals. Lime also yields a basic salt, like baryta, which possesses the same properties as the barytic salt.

Alloxanate of lime is insoluble in alcohol, but more soluble in water than the barytic salt. It yielded—

	I.	II.	III.	Atoms.	Calc.
Carbon	..	..	15.85	8	16.64
Nitrogen	..	..	..	2	9.82
Hydrogen	..	..	4.20	12	4.16
Oxygen	..	..	..	18	49.96
Lime	19.52	19.43	..	2	19.42

It is represented by the formula $C^8 N^2 H^2 O^8, 2CaO + 10aq$.

Binalloxanate of Lime.—The preparation of the acid lime salt is exactly the same as that of the acid barytic salt. A concentrated solution of acid alloxanate of ammonia is mixed with one of chloride of calcium. It crystallizes in transparent deliquescent crystals, which part with the whole of their water of crystallization when dried over sulphuric acid. It dissolves in about 20 parts of water, also in alcohol. The existence of an acid baryta and lime salt must be regarded as the strongest proof of the bibasic nature of alloxanic acid. When dried at 212° , it yielded—

	Calculated.	I.	II.	III.
Lime	15.61	15.34	15.85	15.74
Alloxanic acid	78.38			
Water	6.01			

When dried in the air, it yielded—

	Calculated.	I.	II.
$\left\{ \begin{array}{l} \text{CaO} \\ \text{HO} \end{array} \right\} \text{C}^8 \text{N}^2 \text{H}^2 \text{O}^8$	79.86		
5HO	20.14	20.13	20.21

The formula of the salt, dried at 212° , is $\text{C}^8 \text{N}^2 \text{H}^2 \text{O}^8$, $\text{CaO} + \text{HO}$, of that dried in the air, is $\text{C}^8 \text{N}^2 \text{H}^2 \text{O}^8$, $\text{CaO} + 6\text{aq}$.

Alloxanate of Magnesia.—This salt is prepared in the same way as the neutral alloxanate of lime, by mixing a concentrated solution of chloride of magnesium with one of alloxanate of potash. It crystallizes in crusts, which consist of delicate silky warts. It is tolerably soluble in water, but less so in alcohol. It yielded—

	I.	II.	III.	IV.	Atoms.	Calc.
Carbon	..	..	..	17.84	8	17.60
Nitrogen ..	..	..	..	..	2	10.35
Hydrogen ..	..	..	..	4.68	12	4.37
Oxygen	..	..	..	..	18	52.58
Magnesia ..	14.65	15.11	15.16	..	2	15.10

Its formula is $\text{C}^8 \text{N}^2 \text{H}^2 \text{O}^8$, $2\text{MgO} + 10\text{aq}$.

Alloxanate of Manganese.—The protosalt was obtained by treating a solution of the protacetate or protosulphate of manganese with alloxanate of potash in excess; a copious flocculent precipitate falls; as it is soluble in water, it must be washed with dilute alcohol, the air being excluded. On exposure to the air, it turns brown, deliquesces, and then dries, forming a brown gummy mass, which is readily soluble in water. The white precipitate was quickly dried at 194° – 212° in an atmosphere of hydrogen. It formed a white amorphous powder, which did not alter on exposure to the air even when moistened. This compound was probably composed of mesoxalate of the protoxide of manganese with alloxanate of potash, the alloxanic acid having been partially decomposed. No uniform results could be obtained on analysis; it was constantly found to contain potash. On combustion with oxide of copper, a constant proportion of 1 : 6 in the nitrogen and carbonic acid was observed.

Carbonate of manganese readily dissolves in alloxanic acid, yielding a colourless fluid, which on spontaneous evaporation leaves a crystalline granular salt, which was not examined. Alloxanate of potash reacts upon the salts of cadmium exactly as upon those of manganese, a white precipitate being formed, which also contains potash. Metallic cadmium dissolves in alloxanic acid, hydrogen being evolved and an acid salt formed.

Basic Alloxanate of Zinc.—This salt may be prepared in several ways; either directly from the carbonate of zinc, or by precipitation of the zinc salt with alloxanate of potash. The analyses I., II. and IV. were made on the salt prepared according to the former, and III. according to the latter method. When dried *in vacuo*, it forms a horny elastic mass, which yields a bright white powder. It is very difficultly soluble in water, and forms an acid salt with alloxanic acid. It was analysed after having been dried *in vacuo*, by heating to redness with sulphuric acid, solution, and subsequent precipitation

of the oxide of zinc by carbonate of soda, drying and heating to redness. It yielded—

	I.	II.	III.	IV.	Atoms.	Calc.
Carbon	..	..	..	13.80	8	14.32
Nitrogen ..	..	..	..	..	2	8.53
Hydrogen ..	..	..	..	3.08	10	2.98
Oxygen	..	..	..	..	16	38.17
Oxide of zinc	35.87	35.44	35.97	..	2	36.00

When dried at 212° , it loses 8 atoms of water of crystallization. Dried in the air, it yielded—

	Calculated.	Found.
3ZnO }	78.51	
$\text{C}^8 \text{N}^2 \text{H}^2 \text{O}^8$ }		
8HO.....	21.49	21.39

Hence, dried in the air, its formula is $\text{C}^8 \text{N}^2 \text{H}^2 \text{O}^8, 3\text{ZnO} + 8\text{aq.}$; at 212° , $\text{C}^8 \text{N}^2 \text{H}^2 \text{O}^8, 3\text{ZnO}$.

Binalloxanate of Zinc.—This is obtained by dissolving the above salt in alloxanic acid, or by treating carbonate of zinc with excess of alloxanic acid. By spontaneous evaporation, it at first forms a gummy mass, which gradually assumes a crystalline structure, forming crusts which consist of small warts. It is readily soluble in water and alcohol. It was analysed after drying over sulphuric acid. It yielded—

	I.	II.	III.	Atoms.	Calc.
Carbon	..	..	20.64	8	21.09
Nitrogen	..	..	..	2	12.44
Hydrogen.....	..	..	3.56	7	3.06
Oxygen.....	..	..	..	13	45.73
Oxide of zinc	17.87	17.69	..	1	17.68

Its formula is $\text{C}^8 \text{N}^2 \text{H}^2 \text{O}^8, \text{ZnO} + 5\text{aq.}$

Neutral Alloxanate of Nickel.—This was procured by dissolving freshly precipitated carbonate of nickel in a solution of alloxanic acid. When the solution was dried *in vacuo*, it formed a green gummy mass, which did not subsequently crystallize; on adding excess of alcohol, the neutral alloxanate was precipitated in the form of a green flocculent mass, which was washed with absolute alcohol, pressed between blotting-paper, and dried *in vacuo*. It readily absorbs moisture from the air and deliquesces, but subsequently dries into a transparent green mass, which does not absorb more moisture from the air. The precipitate, dried *in vacuo*, forms a greenish-white powder, which is insoluble in alcohol and æther, and when once dried is unchanged by the air. Water decomposes it into a soluble and an insoluble salt. When dried at 212° , it yielded—

	I.	II.	III.	IV.	Atoms.	Calc.
Carbon.....	..	..	..	19.67	8	18.93
Nitrogen	..	..	..	..	2	11.17
Hydrogen	..	..	..	2.71	6	2.36
Oxygen	..	..	..	..	12	47.90
Oxide of nickel	29.29	29.91	28.26	..	2	29.64

The formula is $C^8 N^2 H^2 O^8, 2NiO + 4aq.$

The soluble compound which is formed by the decomposition of this salt with water, when dried at 212° , is represented by $C^8 N^2 H^2 O^8, 3NiO + HO.$

Alloxanate of the Protoxide of Cobalt is obtained by treating freshly-precipitated protocarbonate of cobalt with solution of alloxanic acid. The solution, when dried *in vacuo* over sulphuric acid, formed a red viscid gummy mass, which at the end of from 5 to 6 weeks had changed into a magma of warty crystals. When washed with water and dried in the air, it formed a rose-red crystalline powder, which was partly soluble in water, but insoluble in alcohol. On drying at 212° , it assumed a bluish-violet colour. The oxide of cobalt was estimated as sulphate. Dried at 212° , it yielded—

	I.	II.	III.
Protoxide of cobalt	20.43	20.68	
Carbon	..	..	22.24
Hydrogen	..	..	1.98

Thus the relation of the atoms of carbon to the protoxide of cobalt is as 6.8 : 1.0, consequently the analysed salt was a mere mixture. It approaches nearest to the acid salt, which requires—protoxide of cobalt, 19.87; C^8 , 25.42; H^2 , 1.58. The excess of protoxide of cobalt and the deficiency of carbon arise from the admixture of neutral salt. Its formula is $C^8 N^2 H^2 O^8, CoO + HO.$

Alloxanate of the Peroxide of Mercury.—This salt is obtained by dissolving the percarbonate of mercury in solution of alloxanic acid, and precipitation with absolute alcohol. The solution is readily decomposed by heat, and deposits a protosalt of mercury. The precipitate thrown down by the alcohol when dry is voluminous, white, pulverulent and insoluble in water. When dried at 212° , it yielded—

	Calculated.	Found.
$2HgO$	60.55	59.68
C^8	13.30	13.10

Dried in the air, it gave—

	Calculated.	Found.
$C^8 N^2 H^2 O^8, 2HgO$	86.81	
$6HO$	13.19	12.55

The formula of the former is $C^8 N^2 H^2 O^8, 2HgO$; of the latter $C^8 N^2 H^2 O^8, 2HgO + 6aq.$

Basic Alloxanate of Lead.—This is obtained by mixing a solution of alloxanic acid with one of basic acetate of lead; a thick white precipitate falls, which is insoluble in water. When dried *in vacuo*, it forms a white pearly powder; when dried in the air, it yielded—

	I.	II.	III.	IV.	Atoms.	Calc.
Carbon	..	..	..	9.78	8	9.87
Nitrogen	..	..	..	..	2	5.82
Hydrogen	..	..	..	0.96	3	0.61
Oxygen	..	..	..	..	9	14.84
Oxide of lead	69.64	68.90	68.80	..	3	68.86

Dried at 212° ,—

	Calculated.	I.	II.
3PbO.....	70.16	70.83	70.33
C ⁸ N ² H ² O ³	29.67		

The formula of the former is C⁸ N² H² O³, 3PbO + aq; of the latter, C⁸ N² H² O³ + 3PbO.

Binalloxanate of Lead.—This is prepared by dissolving recently precipitated oxide of lead in alloxanic acid; the solution, on spontaneous evaporation, frequently dries to a gummy mass, which only crystallizes after the lapse of some time; sometimes the solution readily crystallizes. It forms thick warts, which are made up of silky needles; it is tolerably soluble in water when it has once separated in a crystalline state. It is decomposed into alloxanic acid and $\frac{4}{3}$ -alloxanate of lead by alcohol. Dried in the air, it yielded—

	I.	II.	III.	Atoms.	Calc.
Carbon.....	..	..	17.16	8	17.09
Nitrogen.....	..	..	..	2	10.08
Hydrogen.....	..	..	1.86	5	1.78
Oxygen.....	..	..	..	11	31.33
Oxide of lead	39.78	39.70	..	1	39.72

Dried at 212°,—

	Calculated.	I.	II.
PbO.....	93.54	6.44	6.27
C ⁸ N ² H ² O ³ }			
HO.....			
2HO.....	6.46		

The formula of the former is C⁸ N² H² O³, PbO + 3aq; of the latter, C⁸ N² H² O³, PbO + HO.

$\frac{4}{3}$ -Alloxanate of Lead.—This is formed by treating a solution of acid alloxanate of lead with absolute alcohol; the white caseous precipitate thus formed is deliquescent whilst moist. When dried *in vacuo*, it formed a white powder, which was soluble in acids, partly so in water, being decomposed by it into an acid and a basic salt. Dried in the air, it yielded—

	Calculated.	I.	II.
3PbO.....	48.41	48.67	48.15
2(C ⁸ N ² H ² O ³).....	41.17		
8HO.....	10.42		

Dried at 212°, it yielded—

	Calculated.	II.	III.
3PbO.....	52.51	52.52	52.00
2(C ⁸ N ² H ² O ³).....	44.66		
2HO.....	2.83		

The formula of the former is 2(C⁸ N² H² O³) 3PbO + 8aq; of the latter, 2(C⁸ N² H² O³) 3PbO + 2aq.

Neutral Alloxanate of Lead is left undissolved when the last salt is treated with water. It forms a white powder, which is insoluble in water. Dried at 212°, it yielded—

	I.	II.	III.	Atoms.	Calc.
Carbon	..	..	12.76	8	12.51
Nitrogen	..	..	..	2	7.17
Hydrogen	..	..	1.28	4	1.04
Oxygen	..	..	..	10	21.09
Oxide of lead	58.28	58.59	..	2	58.19

Its formula being $C^8 N^2 H^2 O^8, 2PbO + 2aq.$

Neutral Alloxanate of Copper is obtained by treating excess of recently precipitated carbonate of copper with alloxanic acid; the dark green acid solution thus formed is set aside; it deposits a bluish green precipitate, which is a basic salt. After filtration it is mixed with an excess of alloxanic acid until it assumes a bright blue colour. If a drop or two of the solution is found not to crystallize, more acid must be added. It crystallizes in beautiful blue warts on spontaneous evaporation. It is soluble in 5-6 parts of water; heat turns the solution green. Dried at 212° , it yielded—

	I.	II.	Atoms.	Calc.
Carbon	..	16.61	8	16.34
Nitrogen	..	..	2	9.64
Hydrogen	..	3.17	10	3.40
Oxygen	..	..	16	43.61
Oxide of copper	27.21	..	2	27.01

Its formula is therefore $C^8 N^2 H^2 O^8, 2CuO + 8aq.$

It was analysed by repeated treatment with nitric acid and heating to redness, which caused it to explode slightly.

Basic Alloxanate of Copper.—The manner in which this salt is procured has been described. When dry, it forms a bluish-green powder, which is insoluble in water. Dried at 212° , it yielded—

	Calculated.	I.	II.
$3CuO$	44.02	44.42	44.26
$\overline{Al}$	52.65		
HO	3.33		

All the author's attempts to form an alloxanate of the oxide of ethyle failed.

[To be continued.]

Examination of the Volatile Acids in Viburnum Opulus.

By L. VON MONRO.

Chevreul found in the berries of *Viburnum Opulus* phocenic acid, the identity of which with valerianic acid has been proved by Dumas. Krämer has submitted the bark of *Viburnum Opulus* to examination, and considers the volatile acid obtained from it, as well as its salts, not to be identical with valerianic acid from their external properties. The author was induced to repeat this investigation.

The bark of young trees of *Viburnum* was peeled off in spring, carefully comminuted, and submitted to distillation with water to which some sulphuric acid had been added. 4 lbs. of bark yielded

40 quarts of acid liquid. The distillate was saturated with carbonate of soda and evaporated, when an oil having the odour of *Viburnum* volatilized. The concentrated liquid was again distilled with sulphuric acid to obtain the pure acid; it separated partly in oily drops on the surface of the distillate, and was partly dissolved in it. The drops of oil had the peculiar and strong odour of cheese, as well as the other properties of valerianic acid; the barytic and zinc salts crystallized from the hot solution in pearly laminæ, the silver salt in fine dendritic crystals. The entire distillate was saturated with ammonia and treated with nitrate of silver; it yielded a beautiful white light crystalline precipitate. This precipitate when boiled became black, probably from a small quantity of formic acid which had been formed, but beautifully white crystals separated from the filtered liquid. The first salt which crystallized was that of the volatile acid of *Viburnum Opulus*, viz. valerianate of silver; the salt which separated from the mother-ley was pure acetate of silver.

The valerianate was readily separated from the acetate by recrystallization, owing to its sparing solubility. On analysis it yielded—

Carbon	28.65	10 =	750.0	28.69
Hydrogen	4.33	9	112.5	4.30
Oxygen	11.55	3	300.0	11.47
Silver	55.47	1	1451.6	55.54

The acid discovered by Chevreul in the berries of *Viburnum Opulus* consequently occurs likewise in the bark; and the acid considered as distinct by Krümer is identical with valerianic acid.—*Ann. der Chem. und Pharm.*, iv. p. 330.

On the Products resulting from the Oxidation of Gelatine by Chromic Acid. By Prof. R. F. MARCHAND.

Some time ago Persoz found that gelatine was converted by the action of bichromate of potash into carbonic acid, ammonia and prussic acid; on a repetition of these experiments, however, Mr. Sullivan was unable to detect the latter. The author has also instituted some experiments on this subject, and has obtained very variable results. In the first place, 40 grms. gelatine, as prescribed by Persoz, were dissolved in 1000 grms. water, to which 300 grms. monohydrated sulphuric acid, and after the liquid had cooled, 160 grms. bichromate of potash were added. On heating the liquid, it gave off much prussic acid; what passed over possessed the odour of prussic acid, was distinctly acid, and after some time prussic acid was very readily detected in it. The free acid was formic acid. The distillate contained no formic acid so long as prussic acid passed over; and in proportion as the mixture became concentrated, the quantity of the latter increased, while on diluting the residue formic acid again made its appearance. In a second experiment, which yielded the same results, the author succeeded in obtaining a considerable quantity of cyanide of mercury, together with some formiate of mercury, by shaking the distillate with peroxide of mercury.

The above observation, that an addition of water prevented the formation of prussic acid, and the results obtained by Mr. Sullivan, rendered it probable that by varying the quantities other products of decomposition would be obtained. Instead of the 40 grms. of gelatine, 110 grms. were taken, the proportions of the other substances remaining the same. The consequence was, that no prussic acid was disengaged, but along with carbonic acid very pure formic acid. The author obtained a similar result on distilling cheese, sulphuric acid, chromate of potash and water, in which the cheese was likewise employed in excess.

In the above experiments the odour of bitter almonds always made its appearance before any prussic acid could be detected. This evidently showed that the odour was produced by a second combination, and not merely by the hydrocyanogen. The distillate, agitated with oxide of mercury, also smelt strongly of bitter almonds; and this odour accompanied the liquid even after it had been distilled off oxide of mercury. Nor did the odour disappear on the addition of carbonate of potash, but only after some days when caustic potash had been added to it. The liquid was now evaporated, and the dry saline mass, consisting principally of carbonate of potash, boiled several times with absolute alcohol. The extract was evaporated in the water-bath, dissolved in a little water, and decomposed by hydrochloric acid. From the turbid liquid, which had become clear by the next day, large crystals of benzoic acid were deposited after the lapse of some time. No analysis could be made of them; but the fusibility, volatility, form, and mode of origin from a liquid which had the odour of oil of bitter almonds, and which had disappeared after the separation of the crystals, leaves no doubt that the production of oil of bitter almonds by the oxidation of an animal substance, actually occurred in this instance. When the alcoholic extract of the liquid to which potash had been added and evaporated, was treated immediately with hydrochloric acid, it evolved a distinct odour of butyric æther.

Liebig has shown that a certain quantity of hippuric acid occurs in the healthy urine of man. We are undoubtedly inclined to ascribe its origin to the consumption of certain vegetable substances; however, the well-known amount of hippuric acid contained in the urine of very young children speaks against this view, if we do not derive it from milk-sugar. From the above experiments however it follows that we are also able to produce hippuric acid from the consumed animal substances.

As is well known, hippuric acid has been considered as a conjugated acid in which benzamide is united to an organic compound, say fumaric acid. When the benzoic acid is converted into hippuric acid in the animal body, being transformed into benzamide and combining with the substance C^4HO^3 , there must necessarily originate 1 equiv. of hippuric acid from an equivalent of benzoic acid. The reaction however might also result so that the compound experienced a total change in the organism, and that only oxygen, hydrogen and nitrogen were added to the elements of the benzoic

acid without the carbon being increased, so that only 14 equiv. hippuric acid would originate from 18 equiv. benzoic acid. This may be decided by experiment, as in the first case 1 grm. benzoic acid should yield 1·467 grm. hippuric acid; in the second, 1·141 grm. When the author took at one dose 5 grms. benzoic acid, he found on the next day only 5·12 hippuric acid. According to calculation he ought to have obtained in the first case 7·335 grms.; in the second, 5·705. However, an attack of diarrhoea occurred at the same time, which evidently had interfered with the reaction. He now took 30 grms. benzoic acid in 10 days, and found in their stead 39·2 grms. hippuric acid. According to calculation he should have obtained either 44·01 or 34·23 grms.; consequently more had been found than the latter assumption admits of. The excess cannot be ascribed to the normally secreted hippuric acid, as its quantity is too small.—*Journ. für Prakt. Chem.*, xxxv. p. 305.

Examination of Bees-wax. By Ch. GERHARDT.

According to Lewy, the constituents of bees-wax differ from those of the ordinary fats only by a higher or lower degree of oxidation. According to him, wax may be converted into stearic acid by the fixation of oxygen. However, the author does not agree with the formula which Lewy has advanced for wax, but prefers the formula $C^{19}H^{19}O^{2*}$, which agrees far better with all the analyses hitherto made of it, and by which it becomes analogous to margaric, æthalic, myristic, butyric and acetic acids, &c. The analyses of stearic acid upon which this formula is based are the following:—

Chevreul.		Redtenbacher.					
Carbon	76·4	76·5	75·4	75·8	75·6	75·8	
Hydrogen	12·4	13·0	12·8	13·0	12·6	12·8	
Stenhouse.				Erdmann.			Lewy.
Carbon	75·8	75·6	75·9	76·3	76·7	76·5	76·73
Hydrogen	12·7	12·8	12·8	12·8	12·8	12·8	12·86

The above formula requires 76·5 per cent. carbon and 12·8 hydrogen.

Dry Distillation of Wax.—The author observed, in the destructive distillation of wax, the same phenomena in general as already described by Ettling; a white granular solid mass condenses in the recipient, and floats in a fluid oil, and during the whole of the operation a mixture of carbonic acid and olefant gas is disengaged. The solidified body consists of a fatty acid, a solid and several liquid hydrocarbons. The first portions of the distillate may be almost entirely saponified, and only a few particles of the solid hydrocarbon float in the liquid. By decomposition of this soap with muriatic acid, a perfectly white fatty acid was obtained, which after being purified by recrystallization from a mixture of alcohol and æther, fused

* C = 75, H = 12·5.

at 140° , and solidified on cooling to a radiate mass. Analysis proved it to be *margaric acid*, viz.—

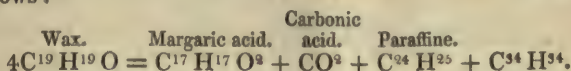
Carbon.....	75.1	17 =	1275.0	75.6
Hydrogen	12.8	17	212.5	12.6
Oxygen	12.1	2	200.0	11.8

The solid hydrocarbon obtained in the distillation is, according to Ettling, paraffine, which consists, according to some recent experiments of Lewy, of $C^{20}H^{21}$, or $C^{24}H^{25}$, which latter formula is most probable when considered with the boiling-point of paraffine. If the oily carburetted hydrogen obtained in the above distillation is treated with a solution of caustic potash, much margaric acid is removed, the previously acid products become neutral, distil readily on rectification, and leave a solid residue of paraffine. The oil rectified once is generally yellow or greenish; it is however easily obtained colourless by distilling it with potassium after desiccation over chloride of calcium. The author regards the oil as a mixture of several isomeric hydrocarbons, for its boiling-point gradually rises from 322° to 396° ; Ettling's product however boiled at 266° . One of these oils, whose boiling-point rose rapidly to 414° , when it remained constant, yielded on analysis—

Carbon	85.4	1 =	75.0	85.7
Hydrogen	14.6	1	12.5	14.3

Two other samples, which boiled at different temperatures, gave the same results. The density of the vapour was found to be 5.52, which corresponds to the formula $C^{19}H^{12}$. Chlorine does not remove any hydrogen from this oil, which circumstance confirms its identity with olefant gas.

In the dry distillation of stearine, the same mixture of hydrocarbons is obtained. The boiling-point of the oil, distilled over potassium and rectified, commenced at 374° , and gradually rose to 464° . The analysis yielded 80.0 per cent. carbon and 14.6 per cent. hydrogen. The formula for wax, advanced by the author, corresponds entirely with its products of decomposition, which may be expressed as follows :—



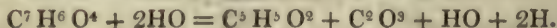
Products resulting from the Action of Nitric Acid.—When wax is boiled with nitric acid, the same phenomena occur as in the action of this acid on stearic acid or other fatty bodies. Much nitrous vapour was disengaged, and the residue, after 2 hours' boiling, dissolved entirely in a hot solution of carbonate of soda. On cooling, the whole solidified, forming a greasy soap of a yellow colour. After 24 hours' boiling, the wax had completely dissolved in the nitric acid; an oily body floated on the solution, which had the odour of rancid butter, and dissolved completely in potash. It reacted acid, and possessed all the properties of *azoleic* or *xenanthylic acid* of Laurent, which is formed in the oxidation of stearic acid and other fatty bodies

When wax was boiled for several days with twice its weight of nitric acid until all the oily substances had disappeared, *pimelic acid* first crystallized; this yielded on analysis—

Carbon.....	52.0	7	= 525.0	52.5
Hydrogen	7.9	6	75.0	7.5
Oxygen	40.2	4	400.0	40.0

The mother-ley yielded a tolerable quantity of hemispherical warts of *adipic acid*, which however were without doubt mixed with some *lipic acid*. The latter acid was also obtained in acicular crystals on evaporating the fluid; the last mother-ley yielded no further crops of crystals, and was rendered turbid by the addition of water, from the separation of oily azoleic acid.

When, finally, wax was boiled with nitric acid until no more red vapours were disengaged, beautiful crystals of succinic acid were formed. It is evident therefore that the products of decomposition of wax are identical with those obtained from the fats. The author observed, that when pimelic acid was fused with hydrate of potash, at first much water, and subsequently, at a somewhat elevated temperature, hydrogen gas were liberated. The residue becomes somewhat yellowish, and yields on distillation with sulphuric acid a volatile acid having the odour of valerianic acid. The collected liquid was saturated with ammonia and precipitated with nitrate of silver; the precipitate became quickly black by exposure to the light. Another portion of the residue, on being carefully saturated with nitric acid and treated with chloride of calcium, gave a precipitate of oxalate of lime. Supposing the volatile acid to be valerianic acid, the reaction would be as follows:—

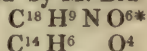


Suberic, adipic and azoleic acids behaved in the same manner. The volatile product of the fatty acids had the odour of rancid butter, and gave a white precipitate with salts of silver, which became black on boiling. It probably likewise contained formic acid.—*Ann. de Chim. et de Phys.*, xv. p. 236.

Further Researches on Hippuric Acid, Benzoic Acid and Sugar of Gelatine. By M. DESSAIGNES.

Hippuric acid has already been the object of many investigations; nevertheless its metamorphoses, already so interesting, still deserve examination. When dissolved in boiling hydrochloric acid, the hippuric acid, as observed by M. Liebig, crystallizes on cooling without alteration; but if the ebullition is continued for about half an hour, the result is very different; it is decomposed, and yields a quantity of benzoic acid equal to that indicated by theory with the exception of a slight loss. The benzoic acid was separated on a filter, and the filtered liquid yielded on evaporation long prismatic crystals, which were acid, contained nitrogen, and into the composition of which hydrochloric acid entered as a constituent part. These crystals were neutralized with carbonate of soda or carbonate of

lead; and after having removed the chlorides from the solution, I obtained different crystals of a very sweet nitrogenous substance, neutral to all tests, and forming crystalline combinations with oxide of silver, and with nitric, sulphuric and oxalic acids. I soon perceived that I had thus produced, by a metamorphosis which might have been foreseen, the sugar of gelatine discovered by M. Braconnot; in fact, if we subtract from



we obtain $\text{C}^4 \text{H}^3 \text{N} \text{O}^2$

to which it is only requisite to add $1\frac{1}{2}$ equiv. of water to obtain the half equivalent of sugar of gelatine, according to Mulder and Bous-singault. However, I am rather inclined to think that 2 equiv. of water should be added to the remainder, $\text{C}^4 \text{H}^3 \text{N} \text{O}^2$, and that the true equivalent of the sugar of gelatine is $\text{C}^4 \text{H}^5 \text{N} \text{O}^4$, as pointed out by M. Gerhardt; but I have as yet no proof to bring forward in favour of this view.

All the reactions, and the very beautiful crystallizations which I have obtained with the saccharine and nitrogenous substance derived from the hippuric acid, and which I have compared with the corresponding reactions and crystallizations of the sugar of gelatine prepared from glue, have convinced me of the identity of these two bodies; but I feel, that in order to impart the same conviction to chemists, the sugar from the hippuric acid must be analysed, and that is what I am about to do. The metamorphosis which gives rise to this body is very precise; no gas is disengaged in the reaction; the two only products are benzoic acid and the hydrochlorate of the sugar. 100 parts of dry hippuric acid yielded—

Dry benzoic acid	67.49
Hydrochlorate of sugar dried over sulphuric acid. .	59.08
	126.57

Nitric acid, after 20 minutes' boiling, converts hippuric acid into benzoic acid, as was known, and into nitrate of sugar or nitro-saccharic acid, which crystallizes in magnificent truncated tablets. The nitro-saccharic acid, prepared with the sugar derived from glue, yielded absolutely the same crystals. I did not collect any gas in this reaction.

Sulphuric acid, diluted with twice its volume of water, equally effects the metamorphosis of hippuric acid, without disengagement of gas and without the liquid becoming coloured. The benzoic acid is readily obtained pure, as is also the sugar of gelatine by saturation of the combination with chalk or carbonate of lead.

I combined sulphuric acid, $\text{SO}^3 + \text{HO}$, with the sugar which I had obtained from the hippuric acid, in equal equivalents, assigning to the latter the formula $\text{C}^4 \text{H}^3 \text{N} \text{O}^4$, and I obtained a solution which crystallized in large prisms of great lustre and to the very last drop.

Even oxalic acid, when boiled for 2 hours with hippuric acid,

converts it into benzoic acid and oxalate of the sugar, which crystallizes in beautiful prisms. Lastly, an excess of potash or of soda, after ebullition for half an hour, equally decomposes hippuric acid into an alkaline benzoate and sugar, which I obtained in the form of hydrochlorate, after having treated the mixture of benzoate and sugar with hydrochloric acid.

Hippuric acid resembles, in these reactions, the amidogen acids, inasmuch as boiling with acids or alkalies restores to it the elements of water, and separates it into an acid and a nitrogenous base, which here replaces the ammonia. I must however state, that I have hitherto not succeeded in combining benzoic acid with sugar of gelatine, consequently in reproducing hippuric acid by causing the benzoate of sugar to part with the elements of water. Sugar of gelatine combines, as above seen, with all the strong acids, and forms very definite acid bodies, which combine with metallic oxides, yielding salts analogous to those double salts of urea recently investigated by M. Werther. I have already prepared a large number of these salts, and have now only to study their properties and submit them to analysis. The evident analogy of urea and sugar of gelatine renders the impropriety of the latter name intelligible; the sugar which I obtained behaves neutral like urea; nevertheless it combines with great facility with acids. These combinations, like the salts of the alkaloid bases, behave as acids, and combine with the metallic bases. Sugar of gelatine has more stability than urea; nevertheless, it is attacked by the continued action of acids. I shall endeavour to discover, by this means, some transformation which will throw more light on its constitution.—*Comptes Rendus*, Dec. 1, 1845.

Experiments to determine the Atomic Weight of Uranium.

By Dr. C. RAMMELSBERG.

The atomic weight of uranium has been stated by Peligot to be 750; however, this number cannot be adopted without very great doubt, because the several experiments of this chemist fluctuate between 689 and 747.5. Wertheim obtained the number 746.36 by the analysis of the crystallized acetate of soda and uranium, and Ebelmen 742.875 from the oxalate of uranium. The former experiments of the author, made with a view to determine the atomic weight of uranium by the reduction of the protoperoxide of uranium in hydrogen, yielded him very variable results, varying between 580 and 736. He has recently employed two different methods, according to the advice of Berzelius:—1st, a weighed quantity of the protoxide of uranium is treated with nitric and sulphuric acid, and the weight of the sulphate of the oxide of uranium determined; and 2nd, this is dissolved with a weighed quantity of magnesia in nitric acid, and converted by ignition into oxide of uranium and magnesium. In the first of these methods the weighing is very difficult, because the weight of the protoxide of uranium always increases some milligrammes on being exposed to the air; moreover the reduction of the protoxide of uranium is constantly accompanied by so lively a

reaction, that a small loss very easily occurs; on evaporation with sulphuric acid, it is difficult to avoid some of the sediment being ejected. In six experiments, where no apparent losses occurred, 100 parts protoperoxide of uranium yielded the following quantities of the sulphate of the oxide of uranium faintly ignited:—

I. 135·76 = 740·545	IV. 136·23 = 729·644
II. 136·094 = 732·77	V. 136·304 = 727·95
III. 139·45 = 661·92	VI. 136·39 = 725·95

Subsequently the author made some experiments with the proto-peroxide, which had been obtained partly by igniting, exposed to the air, the hydrate of the protoxide obtained by ammonia from the protochloride of uranium (VII.); and partly from the nitrate of the oxide by ignition, edulcoration with hydrochloric acid, &c. (VIII.) Neither varied very perceptibly in weight on ignition in oxygen gas:—

VII. 131·79 = 707·33	VIII. 130·74 = 752·35
----------------------	-----------------------

This supposes that the proto-peroxide = UO , U^2O^3 . The employment of magnesia appeared to the author less adapted, because the oxide of uranium and magnesia always decreases somewhat in weight on ignition, from the partial reduction of the oxide:—

IX. 4·713 UO and 0·75 MgO gave 5·739 $\text{U} = 753·757$

X. 3·143 UO and 1·192 MgO gave 4·541 $\text{U} = 662·9$

On repeating the experiments of Wertheim on the double acetates of soda and barytes, the author found that on ignition some traces of the salt evidently escaped as a fine dust as soon as the evolution of gas commenced.

XI. 100 parts acetate of uranium and soda yielded 32·5397 residue, $\text{U} = 743·509$. Anhydrous acetate of uranium and barytes left on ignition the following quantities of BaO , $2\text{U}^2\text{O}^3$:—

XII. 68·38 per cent.; $\text{U} = 644·75$.

XIII. 68·757 per cent.; $\text{U} = 662·997$.

XIV. 68·136 per cent.; $\text{U} = 633·17$.

The most successful experiments yielded numbers situated between 725 and 750, so that the determinations of Wertheim and Ebelmen may undoubtedly be considered as the most trustworthy. —Poggendorff's *Annalen*, lxvi. p. 91.

ANALYTICAL CHEMISTRY.

On the Quantitative Determination of Urea, Potash and Ammonia, in Urine, and on the Composition of the Nitrate of Urea. By W. HEINTZ.

THE method of separating urea by means of nitric acid, proposed by Lecanu, is objectionable for the reasons already stated*, also because there is still doubt regarding the composition of the nitrate. According to Prout, it consists of 1 equiv. of urea and 1 of nitric acid, whilst Regnault finds 1 equiv. of water in addition. Lehmann's analysis corresponds with that of Prout, whilst the author's agrees

* Chem. Gaz., vol. iii. p. 517.

with that of Regnault. On making an ultimate analysis, as Regnault did, the author obtained—

	From urine.	From artificial urea.	Regnault.			
			I.	II.		
Carbon	10·01	9·82	10·04	..	2	9·74
Hydrogen ..	4·11	4·12	4·09	..	5	4·04
Nitrogen ..	34·34	34·57	34·03	34·29	3	34·40
Oxygen	51·54	51·49	51·84	..	8	51·82

In a former number* we gave an account of Marchand's results†, which differ from the above, as he found that when the compound was crystallized from the acid solution, it contained 2 equiv. of nitric acid, 1 of urea and 1 of water. Hence the author was induced to repeat Marchand's experiments. He used the carbonate of baryta for this purpose, and in each experiment prepared the nitrate of urea from a very acid solution. In this manner he obtained 44·14 per cent. of nitric acid only, not 61, as Marchand found. If the nitric acid be calculated for 1 equiv., it requires 43·85 per cent., hence almost exactly the quantity which the author found. As Marchand, in his analysis, dried the substance at 230°–248°, the author supposed that this might have caused a partial decomposition of the salt, and that the result could probably thus be explained. He therefore dried nitrate of urea for some time at 248°, after it had ceased to lose weight at 230°. It then continued progressively to lose weight, and the residue contained ammonia. When however the author dried nitrate of urea at 248° until the loss in weight became barely perceptible, it contained considerably less nitric acid than before, yielding 35·66 per cent., so that Marchand's result could not thus be explained. The author failed to obtain a compound of nitrate of urea containing more than 1 equiv. of nitric acid; hence he draws the conclusion, that urea combines with nitric

* Chem. Gaz., vol. iii. p. 275.

† On a repetition of his former experiment, Marchand could not by any means again procure the same compound. He obtained the anhydrous salt once only; in all other experiments, Regnault's compound. Nor was Erdmann more successful. Werther remarks, that the nitric compounds found by Marchand are very remarkable, since they appear to show that our ideas of the necessity of the 1 equiv. of water, for the urea to combine with as a basic substance, are erroneous, since the compound of 3 equiv. of nitric acid with 2 of urea contains only 1 equiv. of water. Werther found, in four experiments, using carbonate of baryta as Marchand did, in I. 40·56, in II. 41·6, in III. 40·0, and in IV. 31·1 per cent. Werther has also made a series of analyses of oxalate of urea. He did not succeed in obtaining Marchand's hydrated compounds, but once he found a crystalline compound in a solution of oxalate of urea which had been set aside for some time, consisting of 2 equiv. of urea and 1 of oxalic acid. This could not be again obtained. In two experiments, in which he used excess of oxalic acid, he obtained from I. 0·57 per cent. of water and 33·7 per cent. oxalic acid; from II. 0·18 per cent. water and 33·5 per cent. oxalic acid; with excess of urea, he obtained 0·05 per cent. of water and 31·4 per cent. oxalic acid; and with equivalents of urea and oxalic acid, 0·0025 water; after re-crystallizing once, and a second time, the oxalic acid amounted to 33·95 and 33·8 per cent. In drying, the temperature should not be allowed to exceed 257°–266°, for usually, even at this temperature, a sublimate condensed in the cool part of the tube, but its nature was not further examined.—*Journ. für Prakt. Chem.*, xxxv. p. 481.

acid in one proportion only, $\text{NO}^5 + \text{C}^2 \text{H}^4 \text{N}^2 \text{O}^2 + \text{HO}$. 100 parts of this compound contain 48·86 per cent. of urea.

After proving by experiment that in the nitric acid method of estimating the urea there is considerable loss, he proposes adopting the method of determining its quantity from the products of decomposition of the urea, in the manner described by M. Rabsky*.

To ascertain the presence or absence of ammonia in recent urine, the author treated it shortly after excretion with chloride of platinum, adding 3 volumes of absolute alcohol and 1 of æther. The precipitate thus formed was filtered, well-washed with a mixture of æther and alcohol, dried and heated to redness. The residue was repeatedly extracted with boiling dilute muriatic acid, the solution filtered and the filter burnt. The platinum remaining should correspond to the quantity of ammonia and potash in the urine. On evaporating the filtered fluid with chloride of platinum and alcohol, the author obtained a precipitate of platino-chloride of potassium, which was treated as above to estimate the potash it contained. It was found that both potash and ammonia were present†. In his experiments the author obtained very uniform results, viz.—

	I.	II.
Potash	1·315 per 1000 parts.	1·325
Ammonia	2·16 ..	2·19

These small quantities would not interfere with the proposed process; hence it only remains to ascertain whether the other constituents of the urine do not also form ammonia when treated with sulphuric acid. When lithic acid was heated to 356° with sulphuric acid, sulphurous acid was evolved, and the residue contained ammonia. This decomposition cannot however interfere materially, for the quantity of lithic acid present is very inconsiderable, and seldom exceeds 1 part per 1000. Hence also it would be requisite, in accurate analyses, to separate the uric acid by muriatic acid before evaporating the urine with the sulphuric acid. The author next examined the extractives of urine, and found (differently from M. Rabsky) that a small amount of ammonia was formed, as much as would correspond to 0·18 per 1000 of urea, but this quantity is so small that it cannot have any essential influence on the result. The alcoholic extract gives no ammonia with the sulphuric acid.

To estimate the urea by the above-mentioned process, a weighed quantity of urine (6–8 grms.) is treated with about 30 drops of muriatic acid, and set aside in a cool place for 24 hours, then filtered through a very small filter into a large platinum or porcelain crucible; the filter and glass are washed with a small quantity of water; the filtrate is treated with about 6 grms. of sulphuric acid, and the liquid evaporated over a small spirit-lamp, taking care that it does

* Chem. Gaz., vol. iii. p. 518.

† To detect potash and ammonia in urine, Lehmann concentrated it by freezing, but did not obtain any precipitate with chloride of platinum. It is best to treat the urine with the alcohol and æther before adding the chloride of platinum, and to separate the precipitate by filtration. From about 8 oz. of the morning urine, treated in this way, about 10 hours after its evacuation, the author obtained a precipitate with chloride of platinum, which was so small that it could not be further examined.

not boil, until the evolution of carbonic acid commences. The crucible is then covered with a watch-glass and heated until the evolution of carbonic acid ceases, the temperature not being allowed to exceed 180° . The contents of the crucible are then filtered into a porcelain dish, the crucible and the watch-glass are well-washed, and the filtrate is evaporated until almost all the water has passed off. About 20 drops of muriatic acid are then added to the residue, a sufficient quantity of chloride of platinum and alcohol mixed with æther being then added. If the liquid from which the precipitate has subsided is of a very pale colour, more chloride of platinum must be added. After 8–10 hours, the precipitate is separated by filtration, washed, dried and heated to redness in a crucible, which is at first covered, but subsequently open. The residue is treated with boiling dilute muriatic acid, the solution filtered, and this is repeated until the liquid which drops from the filter leaves no residue when evaporated upon platinum-foil; the crucible and filter are dried at a gentle heat; the latter is burnt in the former and weighed. Thus the amount of platinum, which corresponds to that of the potash, ammonia and urea, is obtained.

Another weighed quantity of the fresh urine is treated once with chloride of platinum, 3 volumes of alcohol and 1 of æther; at the end of 10–12 hours the mixture is filtered and the precipitate heated to redness in a well-covered and weighed platinum crucible. The residue is treated as above with dilute muriatic acid, the filter is burned and weighed. We thus obtain the weight of platinum which corresponds to the potash and ammonia contained in the urine; its percentage is calculated, and then deducted from that obtained in the first experiment; the difference gives the amount of platinum which corresponds to the urea.

In estimating the urea, if perfect accuracy be not required, the proceeding previously described* may be adopted, avoiding the separation of the lithic acid, which gives rise to an error of 0.7 part per 1000, placing the average amount of lithic acid in the urine at 1.0 per 1000. The filtration of the residue after the action of the sulphuric acid may be avoided, and it may be mixed at once with the chloride of platinum and the alcohol and æther. The estimation of the amount of potash and ammonia in the urine should not be neglected, as it is liable to considerable variation; the author found it 1.0–11.6 parts per 1000. The resulting error would therefore vary from 0.5–3.5 per 1000. The author thinks this process applicable even in diabetic urine.—Poggendorff's *Annalen*, No. ix., 1845.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Testing of Sodas. By F. P. DULK.

A VARIETY of methods have been proposed for testing the sodas of commerce; the author prefers the following:—Some clear pieces of the soda to be examined are selected free from dust.

* See Chem. Gaz., vol. iii. p. 517.

They are pulverized, well-mixed, and 10 portions, each of 200 grs., weighed off, and preserved in stoppered phials; that each of the five experiments may be repeated. 1. Two of these portions are dissolved in distilled water and neutralized with dilute sulphuric acid. Great care should be taken to attain the point of neutralization as accurately as possible, which is best recognised by tincture of litmus, whereby the two liquids are equally coloured. The liquid appears red before complete neutralization, owing to the carbonic acid dissolved in it; but if it be warmed to remove the carbonic acid, it again becomes blue, and more dilute sulphuric acid must be added to it until no further effervescence results, and the liquid on warming retains a violet colour. This operation is most easily performed in an evaporating dish. By this neutralization with sulphuric acid, not only the carbonate of soda, but also the sulphuret of sodium and hyposulphite of soda, which occur as impurities, are converted into sulphate of soda, while the chloride of sodium is only decomposed with an excess of sulphuric acid. The liberated hyposulphurous acid is immediately decomposed into sulphurous acid, which escapes as a gas, and into sulphur, which at first renders the liquid turbid, but then separates in flakes, and may be removed by filtration. The liquid is now precipitated with chloride of barium, filtered, and the precipitate washed, ignited and weighed. Its weight corresponds to the total weight of the carbonate, sulphate and hyposulphite, as well as of the sulphuret of sodium contained in the soda.

2. Two portions of 200 grms. soda are mixed, each separately, with 400 grms. of pure saltpetre, and melted in a crucible, it being advisable to dry the saline mass previously in order to avoid the effervescence and loss. The fusion may very well be made in a porcelain crucible over an Argand lamp. By this operation both the hyposulphite and the sulphuret of sodium are oxidized into sulphate of soda; and when the fused mass is dissolved in distilled water and an excess of muriatic acid, and then precipitated with chloride of barium, we obtain the sulphate of barytes, both from the sulphate of soda present as such, as well as that formed from the hyposulphite and sulphuret. On subtracting the weight of this sulphate of barytes from that previously found, we obtain the quantity corresponding to the carbonate of soda.

3. The same quantities of soda are treated in the bottles with alcohol of 0.876 spec. grav., frequently agitated, and left for some time in contact; the alcohol, which contains the sulphuret of sodium in solution (when this is present in any quantity, it is coloured yellow by it), is now poured off, evaporated to dryness, the residue mixed with nitre and fused in a crucible. In this case we obtain the sulphate of soda corresponding to the quantity of sulphuret, and its amount may be determined by precipitation with chloride of barium.

4. The sodas from which the sulphuret has been removed by alcohol are dissolved in water and an excess of muriatic acid, and the usually turbid liquid resulting from decomposed hyposulphite of soda heated until the sulphur has separated. The filtered liquid, on precipitation with chloride of barium, yields the quantity of sul-

phate of barytes corresponding to the sulphate of soda contained in the soda. By subtracting it, as well as that obtained in experiment 3, from the weight of sulphate of barytes found in experiment 2, we obtain the amount corresponding to the hyposulphite of soda.

5. Two fresh portions of soda are dissolved in distilled water supersaturated with nitric acid, and warmed until the turbid liquid has become clear, upon which it is filtered and precipitated with nitrate of silver. The chloride of silver, collected on a filter, must be well-edulcorated to remove any sulphate of silver, until what passes through is no longer rendered turbid by muriatic acid.

If the soda should likewise contain lime and iron, they may be separated and calculated according to the usual methods. The author found, on accurate examination, that the method described answers its object perfectly.—*Archiv der Pharm.*, xlv. p. 28.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Dec. 17, 1845. (The President, Professor Graham, in the Chair.)
The following communications were read:—

“New Researches on Aniline,” by Professor Hofmann.

This remarkable liquid, first obtained from the distillation of indigo with caustic potash, and afterwards from coal-tar naphtha, has proved the type of a new class of organic bases, which closely resemble ammonia. The author has extended the analogy between aniline and ammonia by a beautiful series of discoveries, of which the most important are the formation from cyanic acid and aniline of the urea of the latter, and of a new substance which results from the destructive distillation of sulpho-cyanate of aniline. This last is a crystalline sublimate, having the composition of aniline that has lost 1 equiv. of hydrogen, and has assumed in its place a compound of carbon and sulphur, CS, which corresponds in composition to carbonic oxide; it is named carbo-sulphanilide. When treated with an alcoholic solution of potash, the sulphur is exchanged for oxygen, and the true carbonilide obtained. These bodies were also derived by other and more direct means, namely, the first by the action of bisulphuret of carbon upon aniline, and the second by the action of chloro-carbonic oxide gas upon the same substance.

“On Electrical Endosmose,” by Mr. James Napier.

The author commences this first paper of a series on this highly interesting subject with an allusion to Mr. Robert Porrett’s original discovery of endosmose, published in the ‘Annals of Philosophy’ for 1816. In these experiments an extemporaneous diaphragm cell was employed by Mr. Porrett, similar to that now generally in use. After detailing a lengthened series of experiments on this subject, Mr. Napier sums up his general conclusions as follows:—1. That a current of electricity passing through a liquid is always accompanied by a current of the liquid in the same direction. 2. That if the liquid contains a

salt or an acid that is undergoing decomposition, the current is confined to the salt or acid unaccompanied by water, and therefore it does not affect the bulk of the liquid into which it passes. 3. That if the electricity is greater than the salt or acid can conduct, the excess causes a current of the water also to pass.

"Analysis of a Cobalt Ore found in Western India," by Professor Middleton of Agra.

The subject of this paper is found in the hilly district of Rajpottanah, which is remarkably prolific in metallic ores; sulphuret of copper, sulphate of copper and alum being also met with. After detailing the native method of working the copper-mine and the extraction of the metal, the author proceeds to describe the cobalt ore, which is found abundantly in the same mine as a sulphuret of very great purity, in the form of bands and disseminated grains, of a steel-gray colour inclining to yellow. The only substance accompanying it is a highly magnetical iron pyrites, easily separated by the magnet, and in the proportion of 9.22 per cent. The remainder consists of cobalt pyrites, spec. grav. 5.45, and having the following composition:—cobalt, 64.64; sulphur, 35.36; it is therefore a basic sulphuret of cobalt. It is used by the Indian jewellers for staining gold of a delicate rose-red colour.

"Notes on the Preparation of Alloxan," by William Gregory, M.D., F.R.S.E.

In this communication Dr. Gregory admits the error which Schlieper had pointed out in his published process for the preparation of alloxan, as regards the specific gravity of the nitric acid to be employed, which should be 1.4 to 1.42 instead of 1.3 to 1.35, as stated; and proceeds to show experimentally, that with this correction, the process, as originally detailed, is the most productive that has yet been proposed for the preparation of this substance.

"On a new Eudiometric Process," by Professor Graham.

For the rapid absorption of oxygen gas from air and other gaseous mixtures, the author recommends a solution in ammonia of a sulphite of the suboxide of copper and ammonia. This salt falls as a granular brown powder when a stream of sulphurous acid gas is conveyed into a cold solution of the ammoniacal sulphate of copper. When dissolved in ammonia, it absorbs oxygen with singular avidity; and when employed in this form in eudiometry, gives results of considerable uniformity.

PATENT.

Patent granted to John Taylor, of the Adelphi, Middlesex, for Improvements in separating Metals from each other, and from certain Combinations with other Substances.

THE invention has reference to the separation of silver from ores or metallic combinations containing that metal. The patentee first describes the principal methods now in operation for the extraction of silver from its ores and metallic combinations, which are—

1. The process known under the name of the eliquation process, in which the argentiferous substance, whether ore, regulus or metal, is mixed and melted with lead, or some combination of lead, when the silver is obtained in combination with the lead from its great affinity for that metal.

2. The amalgamation process, in which a chloride of silver is formed by mixing common salt with the ore or regulus in calcination, which chloride of silver is again reduced by means of metallic iron and mercury, the chloride passing to the iron, and the silver forming an amalgam with the mercury.

3. A process for which a patent has recently been obtained, the object of which is, the obtaining silver from various known descriptions of copper regulus, procured by smelting argentiferous copper ores, by concentrating the main portion of the silver into a residuum; this is to be effected by thrice-repeated calcination of the regulus, having for its object the formation of as much sulphate of copper as possible, and lixiviation of the sulphated materials with sulphuric acid and water; after each calcination, the undissolved residuum from each of the first two calcinations is to be melted with some material containing sulphur, so as to form it again into a regulus; the residuum of each lixiviation becomes richer from the sulphate of copper and iron being dissolved out, and from only a small portion of the silver being removed as sulphate. When the contents of the first residuum are 100 parts or more of copper to 1 of silver, it is reduced into a regulus by melting with partially calcined copper ore or iron pyrites, and this regulus is sulphated and lixiviated as before, and the product is a residuum containing less than 100 parts of copper to 1 of silver; this is subjected to the same process, and the product is a residuum containing less than 50 parts of copper to 1 of silver; this residuum is called the rich sulphate residuum, and is to be calcined and digested in sulphuric acid, nitric acid and water, and the silver precipitated from this solution; the residuum of this operation is to be added to a residuum containing less than 100 parts of copper to 1 of silver, and melted as above described, or the silver is to be obtained from the rich sulphate residuum by melting it with lead or litharge. A portion of the silver is obtained in each calcination in the state of sulphate, and is washed out by sulphuric acid and water with the sulphate of copper; this silver is to be precipitated.

In describing his invention, the patentee divides it into two parts,—1st, the formation of a chloride of silver, and the dissolving such chloride of silver by any of the hereinafter-mentioned solvents; 2nd, the converting the whole, or practically the whole, silver contained in an ore or regulus into a sulphate of silver by a process of calcination as hereinafter described, the other metals contained in the ore or material treated being rendered insoluble. The sulphate of silver thus formed he dissolves out by hot water.

He then proceeds to describe the means adopted for the attainment of these objects; and first, as regards the chloride process of extraction. The argentiferous materials, which it in all probability

will be desirable to treat, may be divided into two classes,—those containing sulphur, and those containing no sulphur.

First, as regards sulphurous material. If the material to be treated is a regulus of copper or iron, it is preferred first to granulate such regulus by allowing it to flow when hot into water; it is then calcined in a similar furnace to those used for calcining copper regulus, for a time varying from 12 to 36 hours, according to the nature of the regulus under treatment and the quantity in the calcining furnace; 24 hours' calcination for about 3 tons of copper is found to be a very suitable time; during this calcination a moderate fire should be kept up, sufficiently low to prevent the regulus caking; the material should be stirred or turned over once in about every 2 hours. The object of this process is to volatilize a portion of the sulphur, by which means nearly the whole inconvenience arising from the caking of the material in the subsequent calcination is avoided; the regulus so calcined is then ground, and passed through a fine sieve. A sieve of 60 holes to the square inch is well-suited to this purpose. In the same manner, sulphurous ore, which it might be inadvisable to melt from its being already sufficiently rich in silver and needing no concentration, would be most advantageously treated by calcining it as above described previous to grinding it, in order to prevent the formation of lumps in the after-process of calcination; having been calcined, it is then ground to a fine powder, and treated in the following manner, which is equally applicable to calcined regulus. The furnace to be employed is a simple reverberatory calcining furnace, of such size as to enable the workmen constantly to rake the ore lying on every part of it. The heat on the introduction of every fresh charge should be moderate, gradually increasing until it arrives at a bright red heat, approaching yellow; the operation usually lasts from 2 to 3 hours, during which time the material operated on must be constantly raked for the purpose of thoroughly oxidizing the copper, iron and other metals contained in the ore or regulus; a test should now be made of the state of the material operated on; this is done by withdrawing a small portion, and at once, whilst still hot, pouring water on it, and allowing the water to pass through it; should the water appear colourless, or nearly so, the operation of calcination has been carried sufficiently far; but should it be blue or green, the calcination must be persisted in until the green or blue colour disappears from the liquor derived from the lixiviation of a small portion withdrawn from the furnace as described, that is, until the whole of the sulphate of copper and iron has been decomposed. When this has been effected, chloride of sodium (common salt), or any other suitable chloride, is to be added in the proportion of from 4 to 5 parts of salt to 100 parts of the substance treated; a less proportion will do, but to ensure the whole silver being converted into a chloride, the above proportions have been found advantageous. The heat of the substance operated on should be reduced previous to the addition of the salt, in order to avoid a too great evaporation and loss of chlorine. On the addition of the salt the material should be

well-stirred for some time, and a degree of heat maintained sufficient to cause the chlorine or muriatic acid to rise in almost invisible fumes, in which the argentiferous substance should be allowed as it were to soak. A test may now be again made for the purpose of proving whether the calcination has been thoroughly performed; this consists, as before, in withdrawing from the heated furnace a small portion of the substance treated, and pouring over it a hot saturated solution of chloride of sodium (common salt), taking care not to add too much. If this solution is clear and colourless, and becomes, when cold water is added to it, of a whitish colour, the calcination has been complete; but if the solution takes a bluish or greenish colour, the calcination must be continued until the bluish or greenish colour disappears from the solution, and it remains colourless, as above described (when water is added it assumes a whitish colour). The operation may be hastened by strewing over the substance in the furnace another half-pound or pound of common salt for every 100 lbs. of material in the furnace; and the whole must be constantly stirred, as above described. So great is the affinity of silver for chlorine, that it has been found in many instances sufficient to rake the material which has been calcined out of the furnace, and while hot mix it with salt, when the desired chloride of silver has been produced. Should the material it is desired to de-silverize contain no sulphur, or other substance which it is necessary to volatilize or oxidize by such a calcination or calcinations as above described, common salt, in the proportions before given, namely from 4 to 5 of salt to 100 parts of ore or argentiferous substance, may be at once added; and the argentiferous material placed immediately in the furnace, and treated in precisely the manner above described as that adopted for the formation of a chloride of silver in argentiferous regulus or ore, beginning from the point at which the addition of common salt is directed. The addition of a small portion of sulphurous material, such as sulphurous copper ore, iron pyrites or sulphate of copper, has been found to facilitate this operation. A chloride of silver having been thus formed, the argentiferous ore, or substance prepared as above, is to be washed or lixiviated with a hot saturated solution of chloride of sodium (common salt), or any other suitable chloride, alkali or earth, or with a solution of hyposulphite of soda, of hyposulphite of potash, or any other suitable hyposulphite of an alkali or earth which will dissolve the chloride of silver, separating it from the insoluble portions of the material treated. From this solution the silver may be precipitated by any of the known methods; precipitated copper has been found an exceedingly good means of effecting this operation. The heat at which it has been found most advantageous to employ chloride solutions is their boiling-point, or at least 60° R. or 170° F. The temperature of the solution is necessarily effected by the temperature of the substance when subjected to lixiviation. Hyposulphite solutions need not be so hot, as their solvent power is greater.

To ascertain that all the silver has been precipitated, a piece of bright copper, or new copper coin, may be put into the solution in

the precipitating vessels. If these maintain their colour, the liquor may be drawn off, as the precipitation may then be considered complete; but if they come out silvered, it may be considered that sufficient time has not been given for the complete precipitation of the silver.

If the material treated has been copper regulus, some chloride of copper will of necessity be in the solution, as also if copper has been used for precipitation. The liquor, in this case, from which the silver has been precipitated, may then be passed into vessels containing iron, free from oxide scale, where the copper will be thrown down, together with any silver which may have remained unprecipitated; and the copper thus obtained may be used for precipitation of silver, as above described. It may be desirable to economize, as much as possible, the salt used in this process, in which case the lixiviated residue may be further washed, and the liquor obtained preserved, together with that obtained from the precipitation, and having been brought up to the point of saturation, may be again used for the extraction of further quantities of silver.

The second part of the invention consists in the conversion of the whole, or practically the whole, silver contained in any ore or regulus into the state of sulphate of silver, rendering the other metals contained in the argentiferous substance insoluble. If the material to be treated is a sulphurous ore or regulus, it is to be operated on precisely in the manner already described above, as regards the preparatory calcination of argentiferous ore or regulus, with the ultimate view of forming chloride of silver. This part of the invention may be considered to begin from the point at which the ore or regulus has been finely pulverized, after the calcination of the granulated regulus or ore. The ore or regulus is then placed in a calcining furnace, which must be well-provided with a current of atmospheric air passing over the substance heated; and the charge should be constantly raked throughout the whole of the operation. This operation lasts generally about 3 hours, and depends entirely on the good management of the furnace and constant attention to the state of the material acted on. At first the heat must not be great; a moderate heat should be continued until the sulphur ceases to rise in thick fumes, and until, by withdrawing a small portion of the material from the furnace, it is ascertained, by smell or otherwise, that the greater portion of the sulphur has been dissipated; after this more heat may be gradually given, until it at length arrives at a full red heat, approaching yellow. This must be done very cautiously, and during the whole operation the following test must be constantly put in practice. A small portion of the material treated is withdrawn from the furnace, and water, free from chlorine, poured on it whilst hot, or hot water must be used; the liquor thus obtained is then tested by adding a few grains of common salt; when the operation is not complete, the liquor, when first obtained, will be bluish, and when salt is added greenish. The silver, when only a small portion has been formed into a soluble salt by the calcination, will simply cloud the liquor when salt is added.

As the operation of calcination advances, the blue and green colour will nearly disappear from the liquor obtained from the test; and when salt is added, chloride of silver will be at once thrown down, falling to the bottom of the liquor in thick white flakes; when this appearance is given by the test, the operation of calcination may be considered to be complete, the whole, or practically the whole, of the silver being in a state of sulphate, the copper and iron having been oxidized, and thereby rendered insoluble. The material may then be withdrawn from the furnace, and lixiviated with common boiling water, care being taken that it shall be free from chlorine, or only contain a trace of chlorine.

If the material lixiviated be sufficiently hot, the water need not be boiling. From this solution the silver may be precipitated by any of the known methods; and the completeness of the operation may be tested by adding a few grains of salt to the liquor taken from the precipitating vessels; if the liquor remains clear the precipitation is complete. The residue obtained from large quantities has been found to vary from 3000 to 2000 parts of copper to 1 of silver, and were therefore practically wholly de-silverized. Regulus or sulphurous ore may also be at once heated in a calcining furnace, having been first pulverized, without any previous calcination, as above described. In this case very slow heat must be given for the first part of the process, during which time the sulphur contained in the regulus or ore undergoes combustion. After a time this combustion ceases, and the process described as the invention for the conversion of the sulphuret of silver into sulphate begins, and may be performed precisely in the manner pointed out to be practised on the regulus already previously calcined and afterwards ground. This is not considered an advantageous manner of working, from its being impossible to prevent the formation of lumps, which must be separated from the fine parts before lixiviation and again ground and calcined; and also from the necessity of passing the calcined material through a sieve, by which the whole benefit of the heat is wasted; also from regulus being much more readily pulverized when granulated and calcined; and from the saving of labour effected by calcining 3 tons, or a large quantity instead of a small quantity, which must be the case if the process of calcination is performed at once. Should it be desired to treat by the sulphate process an ore which in itself contains no sulphur, and at the same time inadvisable to convert it into a regulus, a small portion of sulphur in any shape, such as sulphurous copper ore or iron pyrites, may be mixed with it, so as to afford sufficient sulphur to combine with the silver; it may then be calcined, as before directed, particular attention being paid to the test. For the purpose of lixiviation, a round tub, fitted with a strainer formed of a disc of wood, pierced with holes, a disc of basket-work, and linen drawn over the whole, answers the purpose well; tow being packed round the sides between the strainer and the tub, the liquor runs off perfectly clear.—Sealed April 15, 1845.

THE CHEMICAL GAZETTE.

No. LXXVIII.—January 15, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Researches on Cetraria Islandica.
By Dr. G. SCHNEDERMANN and Dr. W. KNOP.

WE have already noticed that the authors had separated the so-called cetrarine into several bodies, one of which is the cetraric acid*. In preparing this acid, they took advantage of its property of dissolving far more readily in boiling alcohol and carbonate of potash than in pure alcohol. The lichen, cut up into small pieces, is treated in a still with so much strong spirit that the whole becomes thoroughly moistened; to the mixture about a quarter of an ounce of carbonate of potash is added for every pound of spirit, and the whole is then boiled for a quarter of an hour; the liquid is now strained boiling hot through a piece of cloth, and well expressed, upon which the solution is mixed with muriatic acid until it exhibits a slightly acid reaction, and then with 4 to 5 times its volume of water, when a considerable precipitate results, which is collected on a linen cloth and washed with water. When dry, it forms a mass of a greenish colour, which is the more deep the longer the boiling was continued. It contains at least three different bodies besides the green colouring principle of the lichen, namely *cetraric acid*, *lichesterinic acid*, and another substance, which however for the present is designated by C. The separation of these bodies is very difficult, and with respect to the cetraric acid easily accompanied with great loss, owing to the readiness with which it undergoes change.

The mixed precipitate is now exhausted with 8 to 10 times its weight of spirit of 0.947–0.942 spec. grav., and filtered boiling hot as quickly as possible. Boiling spirit of this strength dissolves a considerable quantity of lichesterinic acid, but very little cetraric acid and C, and likewise very little or none of the green colouring principle of the lichen. On the cooling of the filtered brownish-yellow liquid, a large quantity of a crystalline mass separates, which contains the lichesterinic acid in far greater proportion than the first precipitate, mixed with smaller quantities of cetraric acid and C. The presence of these three bodies is readily detected by means of the microscope, the lichesterinic acid forming four-

* Chem. Gaz., vol. iii. p. 364.

sided rhombic prisms, the cetraric acid long needles, and the body C separating in roundish, apparently amorphous granules. The first precipitate is boiled twice more with the weak spirit until very little or no lichesterinic acid is observed in the mass which crystallizes from the liquid. Upon this the crystallized mass, which now contains all the lichesterinic acid, is collected and washed with a little cold weak spirit and dried. The filtered spirit still contains a small quantity of lichesterinic acid in a very impure state, which may be obtained from it by evaporation.

No other means could be discovered for the complete separation of the lichesterinic from the cetraric acid and the body C than boiling the mass with an essential oil, which dissolves the lichesterinic acid, but leaves the other two substances entirely undissolved. The mixture of the three substances is repeatedly exhausted with boiling naphtha as long as this continues to remove anything, care being taken to agitate the mixture frequently, in order to prevent any burning, which readily ensues. It is each time filtered boiling hot, when on cooling a portion of the lichesterinic acid separates and is collected on a filter. To obtain the portion which has remained in solution, the liquid is distilled with water until most of the naphtha has passed over; the residue is freed from the greater portion of the water by evaporation, then boiled with alcohol to dissolve the lichesterinic acid, the petroleum still floating on the top removed, and the lichesterinic acid obtained crystallized by volatilizing the alcohol. However, the distillation of the naphtha is an extremely disagreeable and dangerous operation, the mixture thumping most violently when the acid begins to separate. Perhaps the separation might be better effected by shaking the solution in naphtha with a solution of an alkaline carbonate; this must however be decided by experiment. The lichesterinic acid so obtained has a more or less yellow colour, and smells of naphtha, but may be readily obtained pure by repeated solution in alcohol, treatment with animal charcoal and crystallization. The cetraric acid which remains behind after exhaustion with petroleum, mixed with some of the body C, forms the smaller portion of the total quantity contained in the crude product; it is of a yellow colour, but can be purified according to the methods given below.

The crude precipitate, after exhaustion with weak spirit, consists of cetraric acid, the body C and the green colouring principle. The complete separation of the latter is extremely difficult. Æther with an essential oil, for instance camphor or oil of rosemary, acquires a deep, dark, grass-green colour; at the same time however it removes the last portions of lichesterinic acid which might still have remained behind. It likewise dissolves some cetraric acid, which may however be obtained from it, and indeed tolerably pure, by partial distillation. The extraction with æther must be continued until the green colour of the mass has entirely disappeared; otherwise in the further treatment, some brown products originate from this green body, which contaminate the cetraric acid, and can no longer be separated from it.

The mixture of cetraric acid and C, which has been extracted with æther, has now a grayish-white colour, and is dissolved by boiling in alcohol of 0·863 to 0·833 spec. grav., the liquid treated with animal charcoal, and filtered boiling hot; on cooling, the greater portion of the cetraric acid and C crystallizes; a portion however still remains dissolved in the alcohol, and can be obtained by evaporation; but it is generally of a brownish colour, and difficult to purify. It is therefore most advantageous to employ as little spirit as possible for solution, in order that the greater part may separate immediately on cooling. The mass, if not yet white, is again treated with alcohol and animal charcoal until it is perfectly white. For the further separation of the cetraric acid from the body C, the solubility of the former in alkalies, in which the latter is insoluble, is turned to account; but then we meet with this difficulty, that the cetraric acid dissolved in an alkali is converted with great rapidity, under the influence of the air, into a brown substance, which when formed even in the smallest quantity prevents the cetraric acid from crystallizing, and cannot be separated from it. This may however be effected by employing a solution of bicarbonate of potash, with which the mixture is treated at the ordinary temperature; this solution dissolves the cetraric acid very readily, but not the substance C. The solution is filtered into a vessel containing some muriatic acid, in order that the liberated carbonic acid may prevent the further access of air. More muriatic acid is added to the filtered liquid, when the cetraric acid subsides in thick white flakes, which are separated by filtration, and well-washed with water. They are then dissolved in the least possible quantity of boiling alcohol, when the acid separates on slow cooling in beautiful white acicular crystals. The mother-ley is generally of a faint yellow colour, resulting from the treatment with alkali, and yields on evaporation an impure cetraric acid, whose quantity however is but small if no excess of alcohol has been employed for the solution.

The body C, which remains behind on treatment with carbonate of potash, is thoroughly washed with water. It should not have the least taste; if it is bitter, it still contains cetraric acid. It may be purified by solution in spirit.

I. *Thallochlor**.—This body, which imparts the green colour to the spherical cells of the lichen, is obtained according to the process above described, dissolved in æther. The solution has a beautiful dark green colour. It also contains some cetraric acid, and generally a small quantity of lichesterinic acid, as this cannot be wholly extracted by the weak alcohol advantageously, because it would at the same time dissolve too much cetraric acid. The greater portion of the cetraric acid separates, as above stated, when part of the æther has been removed by distillation. For the further separation of these bodies, the æther is entirely removed, the residue dissolved in boiling spirit, so much water added to the hot solution until it contains no more than 42—

* A far more appropriate term would be *chlorothalle*, which would make it harmonize with *chlorophylle*.—Ed. Chem. Gaz.

45 per cent. of alcohol, and filtered boiling hot. This process is once or twice repeated, by which the whole of the lichesterinic acid is removed. After evaporation of the adherent alcohol, the residue is boiled with the rectified naphtha, which extracts the green body, while the cetraric acid and brown body, which latter is produced by a metamorphosis of the green substance from exposure to the air, remain wholly insoluble. The dark green petroleum solution is submitted to distillation in water until the greater portion of the petroleum has passed over; the residue is placed in a dish, evaporated to dryness, and finally kept for some time at a temperature of 230° to 248° , until the odour of petroleum has disappeared entirely. We have then a dark, almost blackish-green mass, which is semi-fluid when hot, and on cooling is tenacious like wax; it dissolves in æther and strong alcohol with a dark green colour. It is evidently a mixture of the green colouring substance thallochlor with a colourless semi-fluid fat. The former has the properties of a weak acid, and it may therefore be separated from the latter by combining it with a base. If, for instance, the dark green alcoholic solution is well-agitated with dry hydrate of lime, the colour of the liquid becomes gradually fainter, and at last disappears almost entirely, while the lime acquires a yellowish-green colour. After separating the lime by filtration and evaporating the liquid, a clear, still slightly greenish fat is left, which is perfectly transparent and fluid, when warm is of the consistence of lard, when cold exhibits no trace of crystallization, and possesses a rancid, acid taste. By treating the lime compound with an acid, the thallochlor is obtained in green flakes, which again dissolve in æther with a dark green colour. Hydrate of alumina behaves like lime. Free bases however may have a decomposing influence on the fat, which cannot be the case when the thallochlor is precipitated by acetate of lead. A spirituous solution of acetate of lead produces in the alcoholic solution of the green body an abundant flocculent green precipitate, which, collected on a filter, digested with boiling æther, and then decomposed with acetic acid, yields the thallochlor as a brittle mass, which is readily reduced to powder, and is essentially distinct from chlorophylle, from its being little or not at all dissolved by muriatic acid.

II. Cetraric Acid.—Cetraric acid, the cetrarine of former chemists, when prepared in the manner above described, is a loose tissue of shining minute crystals of a brilliant white colour, which appear under the microscope as long needles. This acid possesses an intense and pure bitter taste; it is not volatile, nor does it melt without decomposition; it is almost insoluble in water, yet the latter when boiled with it acquires a faint bitter taste. Boiling alcohol dissolves it readily, and the more so the stronger it is; it crystallizes for the greater part on cooling, being very sparingly soluble in cold alcohol. Æther dissolves but a small quantity of it, and it is perfectly insoluble in fatty and essential oils. It contains no nitrogen, and loses on desiccation at 212° no chemically-combined water. It is burnt with great difficulty; the analyses were therefore made with the employment of oxygen gas, and yielded the following results:—

Carbon.....	60·25	60·06	60·05	34 =	2554·08	60·05
Hydrogen....	4·63	4·64	4·71	16	199·68	4·69
Oxygen	35·12	35·30	35·24	15	1500·00	35·26
					4253·76	

Cetraric Acid and Alkalies.—Both the caustic and carbonate alkalies dissolve the cetraric acid with the greatest ease; acids separate it from these solutions in white flakes. These solutions have an insupportably bitter taste, far surpassing that of the free acid, owing to its sparing solubility. Recently prepared, they are of a bright pure yellow colour, but on exposure to the air they soon acquire a brownish colour, which, especially on the application of heat, very soon becomes dark brown, the bitter taste diminishing in the same proportion; acids now produce a dirty brown precipitate.

Cetrarate of Ammonia.—Solution of ammonia dissolves cetraric acid very readily to a deep yellow liquid of an excessively bitter taste. This solution is altered by exposure to the air far more rapidly than the solution in potash or soda, the yellow colour is changed into brown, the bitter taste becomes less, and acids precipitate a brownish powder. On evaporation with the assistance of heat, the colour becomes dark brown, and at last almost black; it has then entirely lost the bitter taste; when perfectly dried, it forms an amorphous fissured mass, having a shining fracture, and which dissolves in water with a brown colour, disengages ammonia with potash, and yields a blackish-brown precipitate with acids. It is impossible therefore in this way to obtain an ammonia salt; this may be accomplished however on employing carbonate of ammonia and alcohol. By boiling cetraric acid with solid carbonate of ammonia and strong alcohol and filtration, a yellow solution is obtained, which on quick evaporation in a flask yields a reddish-yellow liquid, from which on cooling a yellow powder separates, which presents under the microscope a crystalline appearance, and from which acids separate white cetraric acid. Its quantity however is very small, the greater portion of the salt remaining in solution in the liquid even when it has been reduced almost to a syrup, when it yields with acids a brownish precipitate, so that the acid in it is already modified. It is most advantageous, in order to obtain the ammonia salt in a pure state, to treat the cetraric acid with dry ammoniacal gas. For this purpose dry gas was passed over the cetraric acid, the air having been previously expelled from the apparatus by hydrogen; after the termination of the operation, the ammonia was again expelled by hydrogen, and this by dry air. On the passage of the ammonia the acid acquired a lemon-yellow colour, and the gas was absorbed under lively evolution of heat. The additional weight amounted to 10·2 per cent. of the acid employed. The composition of the salt is accordingly $2\text{NH}^3 + \text{C}^{94} \text{H}^{16} \text{O}^{15}$; calculated according to this formula, 100 parts cetraric acid absorb 10·08 parts ammonia. The beautiful yellow salt removed from the apparatus possessed a faint odour of ammonia, and was placed over concentrated sulphuric acid until it had disappeared. It then dissolved very readily in water to a yellow neutral liquid.

Cetrate of Lead forms a flocculent yellow precipitate, which is wholly insoluble in water. After drying at 212° , it yielded—

	I.	II.		
Oxide of lead.	..	39.68	2	39.60
Carbon	36.31	..	34	36.27
Hydrogen	2.78	..	16	2.83
Oxygen	..	..	15	21.30

A spirituous solution of acetate of lead produces in the alcoholic solution of cetraric acid a yellow precipitate, which has however no constant composition, the amount of oxide of lead varying in the salt prepared at different times between 44.4 and 38.7 per cent.

Cetrate of Silver forms a yellow precipitate, which very soon becomes brown.

According to the above analyses, the cetrates contain 2 equiv. base, and no water is separated from the acid on its union with oxides, a property which it possesses in common with Erdmann's euxantic acid (Stenhouse's purreic acid) and with usnic acid, which latter it moreover resembles in being readily decomposed in the presence of air and alkalies.

[To be continued.]

Determination of the Amount of Ammonia contained in the Atmosphere. By A. GRÆGER.

Although the existence of ammonia in atmospheric air can no longer be doubted, yet it is important to have a direct proof of it and to determine its quantity. The amount of ammonia in the air at various places, for instance in large towns, has probably some influence on the health; and a careful inquiry into these relations would certainly add much to our knowledge of the origin of diseases of the lungs. The author recommends, for the above purpose, Mohr's apparatus, connected with a thin cylindrical vessel containing dilute muriatic acid.

To obtain, in the first place, an expression for the minimum of the amount of carbonate of ammonia in the air, the first experiment was made on rainy days, between the 14th and 17th of May last year, when it might be supposed that the greater portion of the ammonia had been removed by the rain.

After the author had allowed 36 cubic feet of air, at 744.97^{mm} B. and 51° F., to pass slowly through the muriatic acid, the acid liquid was evaporated in the water-bath in a small platinum dish with a solution of chloride of platinum; the residue was extracted with a mixture of alcohol and æther, the insoluble residue collected on a filter, washed, dried and weighed. The author obtained in this way 0.006 gm. ammonio-chloride of platinum = 0.0008466 gm. carbonate of ammonia. Since 36 cubic feet = 1.112 cubic metre at 744.97^{mm} barometric pressure and 51° F. = 1.06 cubic metre at 32° F., it hence results, that under the above conditions 1.000000 part air contains 0.6148 gm., or somewhat more than $\frac{3}{5}$ millionth of carbonate of ammonia.

The author subsequently repeated the experiment during constant dry and warm weather, and obtained nearly the same result.—*Archiv der Pharm.*, xliv. p. 35.

Pyrophorus from Tartar-emetic.

A very dangerous pyrophorus may be produced by igniting tartar-emetic in a closed crucible. In some experiments to prepare pure antimony in Prof. Wackenroder's laboratory, several ounces of tartar-emetic were submitted to a slight calcination. On emptying the carbonaceous residue, which was still somewhat warm, from the crucible into a dish, it took fire in a few minutes, probably by being breathed upon, and was then suddenly projected about the laboratory, forming a shower of fire.—*Archiv der Pharm.*, xliv. p. 187.

On a Series of Double Salts of the Protoxide and Peroxide of Mercury. By THOMAS BROOKS.

Nitrate of the Protoxide and Peroxide of Mercury.—The protonitrate of mercury, as is well known, acquires a yellow colour on being preserved for some time, owing to a partial higher oxidation. The peroxide formed combines with the undecomposed protoxide to a basic double salt. According to Wittstock, this latter salt can be obtained very pure and of constant composition by boiling 1 part mercury with $1\frac{1}{2}$ part pure nitric acid, of spec. grav. 1.2, in a spacious flask until the mercury is entirely dissolved. During this operation the yellow salt commences to be deposited. Now if the temperature of the liquid be kept for some time near the boiling-point, a considerable quantity of the yellow salt is deposited, and subsequently white basic protonitrate of mercury. The salt thus prepared is anhydrous, and loses at 212° only a little interstitial water; at the same time it becomes of a darker yellow at this temperature, but on cooling reassumes its previous colour. The salt may gradually be exposed to a temperature of 392° without being considerably changed; it merely assumes a transitory orange colour; at 392° however it disengages nitrous acid, and leaves at a somewhat higher temperature very pure peroxide of mercury.

It may be readily proved that the protoxide of mercury in the yellow salt is combined with peroxide in the basic state; for if the salt be triturated with chloride of sodium, it gradually becomes brown-red, and if water be then added, peroxide of mercury is detected in the filtered solution by sulphuretted hydrogen. If the insoluble residue be treated with dilute muriatic acid, this dissolves the peroxide and leaves protochloride of mercury. On boiling the yellow salt for some length of time with water, protonitrate of mercury remains in solution, while peroxide and metallic mercury are separated. If, on the contrary, the salt is boiled for some length of time, the air being excluded, it does not become black. The solution then only contains pernitrates of mercury with a trace of protonitrate. The insoluble residue likewise contains both oxides.

If the salt be treated with a solution of caustic potash, the liquid filtered from the oxide contains pure nitrate of potash, which may be obtained in distinct crystals. When cold sulphuric acid is poured over the salt in the dry pulverized state, nitric acid vapours are sparingly evolved after some time. In the course of 24 hours the whole has changed into a white saline mass, which on the application of heat gives off vapours of nitric acid; consequently the acid contained in the salt is nitric acid, and no lower oxide of nitrogen. To analyse the salt, it was treated in the cold with dilute hydrochloric acid, and the liquid filtered from the formed protochloride of mercury acted upon with sulphuretted hydrogen. To render the determination as accurate as possible, the salt should not be employed in too large a quantity, and the application of heat carefully avoided. The attempt to convert the perchloride of mercury into protochloride by formiate of soda gave no accurate result. To determine the nitric acid, carbonate of barytes was digested with the salt and some water, and the barytes precipitated from the filtered solution by sulphuric acid. The analysis yielded the following results:—

Protoxide of mercury ..	45.10	43.89	42.55	42.69	2	43.57
Peroxide of mercury....	43.66	44.49	46.41	44.49	4	45.22
Nitric acid.	12.54	11.14	10.98	10.59	2	11.21

The composition of the salt may therefore be best expressed by the formula $2\text{Hg}^{\circ}\text{O}$, $\text{NO}^{\circ} + 4\text{HgO} + \text{NO}^{\circ}$.

Sulphate of the Protoxide and Peroxide of Mercury.—When the preceding double salt is gently heated with an excess of a solution of sulphate of soda, a sulphate of mercury is formed corresponding to the nitrate. It is of a similar colour, anhydrous, insoluble in cold water, and is not decomposed by boiling water. Hydrochloric acid decomposes it even in the cold, separating protochloride of mercury; the sulphuric acid is removed from the filtered liquid by chloride of barium, the peroxide of mercury by sulphuretted hydrogen. The analysis made in this way yielded—

Protoxide of mercury.....	44.45	44.21	44.50	2	44.88
Peroxide of mercury	46.84	46.84	46.26	4	46.58
Sulphuric acid	8.56	8.60	..	2	8.54

The formula for the compound would be $2\text{Hg}^{\circ}\text{O}$, $\text{SO}^{\circ} + 4\text{HgO}$, SO° .

The basic persulphate of mercury, which is combined in the salt with basic protosulphate, has a different composition from that obtained by treating persulphate of mercury with water (the so-called *Turpethum minerale*); this, as is well known, is $3\text{HgO} + \text{SO}^{\circ}$. Rose has shown that the neutral persulphate is not, as is generally believed, separated, on its decomposition by water, into an acid and a basic salt, but that the water here acts the part of base, and replaces the peroxide of mercury from its weak basic properties.

The author decomposed neutral persulphate of mercury by continued digestion with cold water and evaporation of the filtered solution at a gentle heat. A white crystalline salt separated, which

was purified from the mother-ley by frequent pressure between blotting-paper. In the examination of the salt dried at 212° , it was found to contain 28.04 per cent. sulphuric acid.

A second portion of the persulphate of mercury was decomposed with boiling water, and digested with warm water for 24 hours. After evaporation of the filtered solution, a considerable quantity of a beautiful yellow turpeth was deposited from the hot solution, being apparently soluble in hot water; however, it possessed entirely the composition of turpeth. The liquid filtered from the turpeth was evaporated further, until on cooling a considerable quantity of the white salt had separated in shining scales, which were again freed from the mother-ley by pressure. This salt consisted of 27.82 per cent. SO_3 and 71.37 per cent. HgO , corresponding therefore to the neutral persulphate. From these experiments, it follows that in the decomposition of the persulphate of mercury by water, no acid sulphate, but a neutral salt and free sulphuric acid are obtained. But might not the entire persulphate of mercury be converted, by a sufficiently large quantity of water, into basic salt and free sulphuric acid, so that no neutral salt remained in the liquid, as this has been distinctly proved in the case of nitrate of bismuth?

Phosphate of Protoxide and Peroxide of Mercury.—This salt is formed by the decomposition of the pulverized nitrate of the proto- and peroxide of mercury with a concentrated solution of ordinary phosphate of soda. The salt changes its colour, and becomes of a darker yellow. It is heated faintly, but not to boiling, and washed for a very considerable length of time with cold water. The phosphate of the proto- and peroxide of mercury obtained becomes blackish on the surface on exposure to the air, especially in the moist state; it contains neither nitric acid nor soda. The protoxide of mercury may be determined in the salt by hydrochloric acid, the peroxide by treating the filtered solution with sulphuretted hydrogen. The phosphoric acid may be estimated by igniting the salt with oxide of lead, from the increasing weight of the latter. The salt contains water, which cannot be volatilized at 212° , but only at a temperature at which the salt is completely decomposed. The analysis yielded—

					Mean.
Protoxide of mercury	44.56	44.92	44.67	..	44.72
Peroxide of mercury	45.15	44.65	44.73	..	44.84
Phosphoric acid	4.56	4.72	4.27	4.67	4.55
Water	..	..	..	..	5.89

Although the quantities of phosphoric acid in the above analyses agree very well, this was not the case in samples prepared at different times. With respect to the relative amount of peroxide of mercury, this compound contains less, from a small quantity being dissolved by the phosphate and nitrate of soda of the mother-ley.

When the nitrate of the proto- and peroxide of mercury is treated with a solution of pyrophosphate of soda, it is rapidly decomposed in the cold, and acquires a darker colour than the other double salts. The filtered liquid contains much protoxide of mercury, but

very little peroxide. The salt obtained is readily decomposed by washing with boiling water, metallic mercury being eliminated.

Oxalate of the Proto- and Peroxide of Mercury.—The nitrate was treated with neutral oxalate of potash; no decomposition appeared to result in the cold, but only when warmed to 86° – 120° . The filtered liquid contained neither protoxide nor peroxide. The salt is free from nitric acid, reddish-brown, and is very readily decomposed, even below 212° , into a grayish-brown mass, which contains much metallic mercury. The double salt undergoes this decomposition much sooner than either the protoxalate or peroxalate separately.—Poggendorff's *Annalen*, lxi. p. 63.

Observations on the Ferrocyanide of Potassium. By Dr. F. F. RUNGE.

As the ferrocyanide of potassium is decomposed on ignition, into cyanide of potassium and iron, Liebig has assumed, that on igniting animal charcoal potash and iron, cyanide of potassium alone is formed, and that this is converted into ferrocyanide of potassium on extracting the ash with water. If the finely-powdered fused mass is digested with spirit, but little cyanide of potassium is obtained; on the other hand, on exhausting it with hot water, ferrocyanide of potassium is immediately obtained, and indeed to the same amount as when procured from the ash in the ordinary way. If the formed cyanide of potassium were capable of dissolving iron, the iron extracting-pans ought to be considerably attacked, which however is not the case, as they frequently last more than ten years.—Poggendorff's *Annalen*, lxi. p. 95.

On the Atomic Weight of Chlorine. By CH. GERHARDT.

Since several of the atomic weights have been submitted to a more rigorous examination, with the employment of more accurate methods, the hypothesis of Dr. Prout has been confirmed for a large number of simple bodies. In most cases they have been found to be multiples of hydrogen when the methods were sufficiently simple and direct. The determination of the atomic weight of carbon, hydrogen and nitrogen, yielded in this respect such precise results, that M. Dumas openly declared himself in favour of the hypothesis of the English chemist.

There was however one element for which experiment had constantly given results contrary to this hypothesis; chlorine, successively examined by Berzelius, Marignac and Pelouze, had never led to a multiple in whole number, the results of these chemists always agreeing with the number 35.8, hydrogen being taken as unit.

Struck by this circumstance, I have repeated the experiments of these chemists, employing the same method, *i.e.* calcining perfectly pure chlorate of potash, and determining the weight of the residue of chloride of potassium. I took care to observe in these experiments all the precautions so well described by M. Marignac. Several experiments led me absolutely to the same results, *viz.*

60·871 60·881 60·875 residue per cent. chloride.

I operated on 4 to 5 grammes of substance, and my balance indicated perfectly fractions of a milligramme.

These results, it will be seen, are exactly in accordance with those of Berzelius, Pelouze and Marignac. They however require correction; I observed, in fact, that the precautions described by M. Marignac do not suffice to prevent the current of oxygen gas from carrying with it a certain quantity of chloride, small, it is true, but always sufficient to modify the atomic weight sought for.

I therefore added the following to the precautions already employed: I fixed to the apparatus a U-shaped tube full of moist cotton, and to this tube a second filled with pumice-stone moistened with sulphuric acid, having proved, by some preliminary experiments, that the current of gas did not in this way remove any trace of chloride. This time the experiments, which agreed quite as well as the preceding with one another, gave a weight of chloride perceptibly higher than that previously obtained. The following are the results:—

60·947 60·947 60·952.

Now if we calculate the atomic weight of chlorine from these data, we arrive exactly at the multiple number 36. I should add, that no care has been neglected to render these experiments as accurate as possible, a single operation having always occupied me the whole day.

These experiments furnish further support to the views of Dumas respecting the value of the hypothesis of Dr. Prout.—*Comptes Rendus*, Dec. 8, 1845.

ANALYTICAL CHEMISTRY.

On the Separation of Gold and Platinum from Tin and Arsenic.

By Dr. L. ELSNER.

As a solution of gold is precipitated by protosulphate of iron, which is not the case with perchloride of tin and free arsenic acid, this property affords a simple means of separating these metals from gold; it is also known with respect to platinum, that of the above-mentioned metals it alone is precipitated by a solution of chloride of ammonium. To ascertain in how far the above mode of separation is suited for a quantitative determination of the gold in a common alloy, a mixture of 4·312 grms. platinum, 4·0 grms. chemically pure tin, and 3·156 pure gold, were dissolved in nitromuriatic acid, the solution evaporated to drive off the excess of acid, diluted with distilled water and alcohol, and concentrated solution of chloride of ammonium added to it; the yellow precipitate obtained was collected on a filter, dried and ignited; it yielded 4·281 metallic platinum. The liquid filtered from the ammonio-chloride of platinum was treated with an excess of a recently prepared solution

of protosulphate of iron; the brown precipitate was filtered after a short time, dried, ignited and weighed; it yielded 2.906 metallic gold; the liquid filtered from the gold and acidulated with hydrochloric acid did not yield a pure yellow precipitate with sulphuretted hydrogen, which should have been the case had all the gold been thrown down by the protosulphate of iron, but the colour was brownish-yellow; a solution of protochloride of tin likewise produced, in another portion of the liquid, a beautiful dark red colouring, which however remained transparent. Both these reactions prove that the protosulphate of iron, even when employed in excess, does not precipitate the whole of the gold from its solution.

It was found, on the contrary, that metallic zinc throws down the gold from a solution of the chloride so thoroughly, that the liquid filtered from the brown precipitate, after the addition of a little muriatic acid, did not yield with sulphuretted hydrogen the slightest brown turbidness.

In order to determine the quantity of gold by means of zinc in an alloy of arsenic, tin and gold, containing 3.8 grms. of the latter, the mixture was dissolved in nitro-muriatic acid, and after removal of the free acid, and resolution in distilled water, the above metals were thrown down by zinc as a grayish-black powder, and so completely that sulphuretted hydrogen produced not the least trace of opacity in the filtered liquid. The object in precipitating the metals by zinc was in order to obtain them in an extremely fine state of division, this being absolutely necessary for the further course of the operation.

The metallic powder is perfectly dried in a current of hot air, then conveyed into a glass bulb of a reduction-tube, and a current of chlorine, dried by chloride of calcium, passed over it. Both tin and arsenic yield volatile compounds with chlorine, which is not the case with gold and platinum. The glass tube, curved at right angles, dipped slightly into distilled water which had not been previously acidulated, no further attention being paid to the chlorides which distilled over. The glass bulb was at first heated by the flame of a small spirit-lamp, subsequently over an Argand lamp, to incipient red heat, as long as white vapours were disengaged. After the termination of the operation, the glass bulb was separated by the cut of a file from the remaining portion of the tube, the contents of the bulb dissolved in nitro-muriatic acid, the solution freed by evaporation from the excess of free acid, the residue diluted with distilled water, and the gold precipitated as a brown powder by the immersion of a bar of zinc in the solution; after desiccation and ignition it weighed 3.4 grms., showing a loss of 0.4, which must be ascribed to the number of operations requisite in this method, which is far less simple of execution than that first proposed, and which consequently deserves the preference.—*Journ. für Prakt. Chem.*, xxxv. p. 310.

Simple Method of reducing Chloride of Silver.

Levol gives the following simple method of reducing chloride of silver. It is placed in a solution of caustic potash in which some

sugar is dissolved, and the whole boiled. The silver is quickly reduced by the sugar, carbonic acid gas being evolved, and is easily washed and obtained pure and in the state of powder.—Berzelius, *Jahresbericht*, xxv.

PHARMACOLOGY.

On the Preparation of Alcoholic Tinctures. By J. PERSONNE.

THE objects of the present memoir, for which the author received the prize proposed on this subject by the *Société de Pharmacie*, were,—1st, to ascertain whether the proportion of alcohol at present employed is sufficient to dissolve the whole, or at least the greatest possible amount of the principles contained in the substances; and if not, to determine the best proportion to be used; and 2nd, to ascertain the most suitable degree of strength the alcohol should possess to dissolve the active principles of the materials. In order to determine the amount of alcohol requisite, it was necessary to macerate the substances under examination with variable quantities of spirit, then to obtain the entire amount of the tincture, and to evaporate it in order to obtain the weight of the matters in solution. To accomplish this, pressure was first tried; but this was soon found to be insufficient, the same operation, repeated several times with the same proportions of solvent and substance, having constantly yielded widely different results. The author found the following process to answer best:—A weighed quantity of substance was macerated during a suitable time in a given proportion of alcohol; the maceration being completed, the whole was brought upon a filter, the quantity of filtered tincture accurately weighed, then evaporated in the water-bath, and finally the extract obtained dried in a chamber heated from 158° to 194° , until it no longer altered in weight. The weight of this extract, subtracted from that of the evaporated tincture, yielded the weight of alcohol contained in that quantity of tincture; a simple equation then suffices to ascertain the total weight of extract which the whole of the tincture would have yielded.

15 grms. of cinnamon, for instance, were macerated with 5 parts or 75 grms. of alcohol of 0.865 spec. grav.; the weight of the tincture which passed through the filter was 27.08 grms.; that of the extract obtained from this quantity of tincture, and dried completely, was 0.94 grm.; subtracting this from 27.08, we obtain 26.14 for the weight of alcohol contained in the quantity of tincture evaporated. The following proportion, $26.14 : 0.94 :: 75 : x$, then gives the total weight of the substance which the whole of the alcohol had dissolved: $x = 2.69$ grms. extract.

In order to ascertain the strength of the alcohol most favourable for the preparation of tinctures, the author determined the quantity of the active principles contained in the substances where they were

well-defined and characterized principles; such, for instance, was the case with the barks, *nux vomica* and *jalap*. These determinations were made in the following manner:—For the barks and the *nux vomica*, the tincture was evaporated in the water-bath, and the extract obtained treated with acidulated water; the filtered liquid was precipitated by subacetate of lead to remove all foreign matters; and the excess of lead having been separated by sulphuretted hydrogen, the alkaloids were thrown down by a solution of pure tannin, and estimated in the state of tannates.

In the case of *jalap*, the resin was extracted from a given quantity of tincture.

But although, for the above substances, the results may readily be checked, it is not so for the greater number, the active principles of which do not possess well-defined chemical properties. How, for instance, in the case of hemlock, belladonna, rhubarb, gentian, &c., is it possible to determine whether the tincture prepared with alcohol of 0·865 contains more active principles than that prepared with alcohol of 0·923? Among these substances, there are some, the properties of which reside in a bitter principle, as rhubarb, gentian, wormwood. In such cases the author took two fixed quantities of tinctures, prepared with alcohol of different degrees, and ascertained by diluting them, which required the greater quantity of water for the bitterness to disappear.

Unfortunately these means of investigation cannot be employed for a very large number of substances, a defect which it has not been found possible to remedy; it is only by reasoning, founded on the chemical analysis of these substances, that the author has selected the degree of alcohol suitable. The only method, in his opinion, of arriving at the desired object, would be to experiment in practice with tinctures prepared from such substances and alcohol of different degrees of strength.

The degrees of alcohol employed in these experiments are five in number, viz. alcohol of 0·833, 0·865, 0·889, 0·923, and 0·942 spec. grav.

From the experiments detailed, amounting to no less than 300, upon 32 different substances, the author considers himself justified in drawing the following conclusions:—

1. The different degrees of strength of alcohol prescribed by the French Codex (0·848, 0·865, 0·923) are not always the most favourable for dissolving the greatest quantity of the principles contained in the substances employed in the preparation of tinctures.

2. These degrees can scarcely be admitted in a general manner, except for a certain number of substances; experiment alone can show which is best suited for each.

3. The proportion of 4 parts of alcohol to 1 of substance, as prescribed in the Codex, is scarcely sufficient in any single case to dissolve all the soluble parts of the substances.

4. The quantity of alcohol sufficient to exhaust a substance entirely is in general 5 parts of alcohol to 1 of substance. In certain cases however, which are nevertheless rare, this proportion is not

quite sufficient ; but the quantity of matter dissolved is so slight, that it may be neglected for the sake of making the rule general.

5. The quantity of alcohol is always sufficient to exhaust a substance when this vehicle is in sufficient quantity to moisten it thoroughly, and when the substances are of an herbaceous nature, as leaves, &c.

6. The alcohometric degrees most suitable for the preparations of the different tinctures are alcohol of 0·865, 0·923 and 0·942 spec. grav.

These alcohometric degrees are arranged in the following table with the substances for which they are suited. To each of the tinctures is added the quantity of substance equivalent to 1 grm. of tincture.

In concluding, the author mentions a singular fact which occurred in nearly every experiment ; almost every time that the proportion of alcohol was greater than required to exhaust the substances, he always obtained less extract than when the proportion was just sufficient ; that is to say, the quantity of extract diminished in proportion as the quantity of alcohol was increased.

This fact is analogous to that which is equally observed when water is added to a concentrated solution of opium, and the substances which were previously held in solution are precipitated. It shows that it would be highly inconvenient to increase to any extent the proportion of alcohol in the preparation of tinctures ; for besides the density of the tincture being diminished by this addition of alcohol, it would likewise be so from a precipitation of a certain quantity of matter, as occurs with the solution of opium.

Table of the different Degrees of Alcohol to be employed for each Substance.

		In round numbers.	
Take 1 part of substance and 5 parts alcohol of 0·865 spec. grav. for the tinctures of	Yellow bark	1 grm. equiv. to 0·20 powder.	
	Jalap.	1 ..	0·19 ..
	Cinnamon	1 ..	0·20 ..
	Pyrethrum	1 ..	0·20 ..
	Castor	1 ..	0·18 ..
	Myrrh	1 ..	0·19 ..
Take 1 part of substance and 5 parts alcohol of 0·923 spec. grav. for the tinctures of	Rhubarb	1 ..	0·18 ..
	Gray bark	1 ..	0·20 ..
	Ipecacuanha	1 ..	0·19 ..
	Nux vomica	1 ..	0·20 ..
	Gentian	1 ..	0·18 ..
	Red bark	1 ..	0·20 ..
	Digitalis	1 ..	0·18 ..
	Senna	1 ..	0·19 ..
	Squills	1 ..	0·17 ..
	Black hellebore. . .	1 ..	0·18 ..
	Contrayerva	1 ..	0·20 ..
	Polygala	1 ..	0·18 ..
	Ginger	1 ..	0·20 ..

		In round numbers.	
Take 1 part of substance and 5 parts alcohol of 0·942 spec. grav. for the tinctures of	Valerian root. . . .	1 grm. equiv. to	0·19 powder.
	White hellebore 1	...	0·18 ...
	Colchicum (corms) 1	...	0·19 ..
	Aconite	1	0·19 ...
	Hemlock	1	0·18 ...
	Belladonna	1	0·19 ...
	Hyoscyamus	1	0·18 ...
	Stramonium	1	0·18 ...

With respect to the mode of preparing these tinctures, the author considers that it has been clearly proved, that of all the methods proposed that of cold maceration is the most suitable.—*Journ. de Pharm.*, Dec. 1845.

Chemical Examination of several Species of Meloe.

By J. LAVINI and M. SOBRERO.

The fluid which the several species of *Meloe* excrete when touched has, as is well-known, a similar effect to cantharides. It has long been the custom to submit the living animals to pressure in Sardinia, and to employ the expressed fluid when mixed with fat to form an epispastic ointment.

The authors exhausted the coarse powder of several species which occur in Piedmont (*M. violaceus*, *M. autumnalis*, *M. Fucia*, *M. punctatus*, *M. variegatus*, *M. scabrosus*, and *M. majalis*), first with boiling water, and then with alcohol and æther. The aqueous solution, which possessed acrid properties, was evaporated to the consistence of a thin extract, and then treated with æther. The solution was colourless, and deposited on spontaneous evaporation white prismatic crystals, which were identical with cantharidine. When pure, they were insoluble in water, soluble in æther, especially when boiling, in alcohol, sulphuric acid, nitric acid, solution of potash, but insoluble in muriatic acid. They also dissolved in acetic acid, especially on the application of heat—a property which likewise belongs to cantharidine. They fuse, when heated on platinum foil to 410°, giving off white vapours; at a higher temperature they are decomposed and burn with a white flame, leaving a readily combustible cinder. The analysis yielded 61·77 per cent. carbon, 6·30 hydrogen, and 32·53 oxygen—results which agree sufficiently with those of Regnault, obtained in the analysis of cantharidine.

The powder which had been exhausted with water, and from which the æthereal extract had been obtained, yielded a small quantity more cantharidine, a green oil easily soluble in alcohol and æther, which possessed acid properties, expelled carbonic acid from the alkaline carbonates, and formed soaps with them; moreover, a yellow oil, soluble in æther, but almost insoluble in alcohol; and finally a white volatile substance, crystallizing in warty masses and soluble in very dilute alcohol. When the substance which had been treated with æther was extracted with alcohol, it yielded mere traces of the substances soluble in æther, already mentioned.—*Journ. de Pharm. et de Chim.*, vii. p. 467.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Coppering by Galvanism without the Employment of Cyanide of Potassium. By Dr. L. ELSNER.

THE author has found, after numerous experiments, that a coppering liquor may be readily and cheaply obtained by the following process.

A given quantity of pulverized white bitartrate of potash is boiled in a porcelain basin, or in an enamelled cast-iron vessel, with about 10 times its weight of rain-water, and to the liquid so much recently-prepared hydrated carbonate of copper which has been washed with cold water added, that a portion of it remains undissolved as a basic greenish-blue powder, and the beautiful dark blue liquid has an alkaline reaction upon reddened litmus-paper. The liquid filtered from the undissolved cream of tartar and hydrated oxide of copper forms the coppering liquor; it is well to render it strongly alkaline by the addition of a small quantity of carbonate of potash. The deep dark blue liquid thus prepared contains in solution the double salt of tartrate of potash and copper, and may be preserved ready prepared without the least danger of alteration. The hydrated carbonate of copper required for the preparation of the above double salt is obtained by mixing a solution of sulphate of copper with a solution of carbonate of potash; a blue precipitate forms, which is collected on a filter or strainer and well-washed with rain-water.

This liquor is employed in the usual way; the copper employed as positive electrode dissolves readily in it, so that the solution is kept constantly at the same degree of concentration. A comparatively weak current, and perfect contact of the objects to be coated with the copper wire coming from the zinc pole, are requisite conditions for the operation to succeed well.

I have coppered tolerably large objects of cast iron, zinc and tin with the above coppering liquor. The colour of the coated objects is quite the same as with a cyanide of potassium solution; the above liquor therefore replaces in every respect this highly poisonous and readily decomposable preparation, the expense moreover of which bears no proportion to that of the perfectly innocuous cream of tartar, which may moreover be had everywhere. The advantages of this copper liquor, in comparison to that prepared with cyanide of potassium, are self-evident, especially if we consider that large objects have hitherto been rarely coppered on account of the high price of the cyanide of potassium. Cast iron or zinc statues, and large objects made of tin, may now be coated cheaply with copper, and in this way replace those obtained by electro-precipitation, which are far more expensive.

Before concluding this notice, I may observe, that it sometimes happens that the objects during the operation become variegated, a circumstance which generally occurs when the current is not properly in order. To remove this coloured coating, it is only necessary to take the object out of the liquor, and to wipe it with a cloth

moistened with a little very dilute muriatic acid, which readily removes the coating.—*Journ. für Prakt. Chem.*, xxxv. p. 361.

On Cochineal. By AUGUST FABER, Esq.*

On board the "Tay" West India steamer, in which I came out, there was also as passenger, Mr. Innis, merchant, going out to Vera Cruz. His residence is in the city of Oaxaha (pronounced *Oaxaka*) in the province of that name, where chiefly cochineal is grown. The following information, which I obtained from him, is in several respects very interesting:—

1. "Silver cochineal is the impregnated female just before laying eggs; black cochineal is the *female after laying and hatching the eggs*."

2. "The female, just before laying the eggs, spreads out a large quantity of white powder immediately around her, and to a great distance, in a circle; and the Mexican growers are in the habit of blowing this white powder off the plant as much as possible, saying the young do better without it."

Now we begin to know something of the origin of the difference of colour and shape and *quantities*, in this way: the black, if good, is always *shelly*, the real silver is *never* shelly; and of black cochineal, there is never more than one bag in twenty, or in thirty, or fifty imported, being in fact only what had been kept for seed.

The last quotation given above would suggest to me one more possible fact.

Why, I would ask, is the Honduras cochineal (which, in fact, grows in Guatemala) *invariably brilliant* in colour (silver), while the Mexican is *invariably* dull, the latter fetching 3*d.* and 4*d.* per lb. less than the former? I consider it very probable, that the habit of blowing off what is given by nature, namely the white powder deposited by the females, may be the reason not only of the dulness of the colour, but also of the generally smaller grain.

3. Mr. Innis told me further, that the more extensive cultivators never kill the insect by immersion, but only by the basket being placed in heated rooms or stoves. The smaller and poorer cultivators use hot water, "by which the insect is mostly burst open, and the 'foxy' colour produced."

"Foxy" is the technical London name for silver cochineal, rather reddish, and very different from the fine transparent red, which forms the finest black.

As I am upon this article, I beg to add a few remarks, more strictly commercial:—

1. The serons in Guatemala are made up to 150 lbs., a mule *there* not being able to carry more than 300 lbs. over the mountains. In Vera Cruz, the distance from shore is 300 miles, but not being so mountainous, the mules carry 400 lbs., the serons being made one-third larger than at Guatemala.

* Extracted from a letter dated "Madeira, October 18, 1845," addressed to Dr. Pereira; and read before the Pharmaceutical Society.

2. In London, every seron of cochineal, on its arrival, is turned out and sifted by the dock companies, filled into English bags, on which the tare to the ounce is marked, the dust of a whole parcel (of 100 to 500 bags) being put together and sold separately from the grain. The invariable custom of sifting exists in no other port than in London.

3. There still exists as an article of commerce, but only just still exists, the sort called "English-dyed black cochineal."

When, in 1826, I established myself in London, this article was extensively shipped to India, Russia and Austria, and for a number of years my Price Current had the quotation of "English black cochineal;" and, in fact, being cheaper in many places, they would not have the genuine black. It was Mexican silver grain *dyed*, and prices were about the following:—Genuine black, 6s. 6d.; English dyed, 5s. 6d.; Honduras silver, 5s. 6d.; Mexican silver, 5s.

Note added by Mr. Wood, Mr. Faber's Clerk.

Granilla is imported from the same places as the cochineal, namely Honduras and Mexico, and consists of the very small immature insects. Its value is from 2s. to 4s. per lb. according to quality.

Garblings consist of the broken pieces of the insects, mixed with the dust and extraneous substances that must of course be gathered with the insects in taking them from the plants. As garblings contain generally a good proportion of the broken particles of matured insects, they are frequently preferred to granilla, unless the latter be of unusually good quality. The value of garblings is 2s. to 2s. 6d. per lb. Each bag of cochineal is sifted here on importation, and it is in this manner that the garblings are obtained, as they are seldom imported so.

The following is a table of the quantities of cochineal exported from and consumed in England in the last 12 years:—

	lbs.		lbs.
1833.	309,125	1839.	1,010,193
1834.	405,350	1840.	1,330,295
1835.	516,132	1841.	1,439,742
1836.	604,425	1842.	1,207,920
1837.	517,882	1843.	1,457,456
1838.	536,044	1844.	1,569,120

Pharmaceutical Journal, Jan. 1846, p. 312.

Adulteration of Iodine.

M. Herberger draws attention to the fact, that with the present high price of iodine sophistications are uncommonly frequent. Thus he found in one sample native sulphuret of antimony. But the adulteration with artificial graphite is far more deceptive; it may however be readily detected by driving off the iodine at a gentle heat, and subsequently raising the temperature with access of air. In one instance the author found no less than 51 per cent. of graphite.—*Jahrb. für Prakt. Pharm.*, xi. p. 35.

PATENT.

Patent granted to William Newton, Chancery Lane, Middlesex, for Improvements in dyeing Cotton, &c.

THESE improvements consist principally in the production of sulphuret of lead, which is effected,—1st, by means of one of the mordants of lead hereafter described (the novel application of which to the purpose of dyeing constitutes one improvement); and 2nd, by the employment of sulphuret of calcium.

Sulphuret of calcium is obtained by boiling quick lime with flowers of sulphur. The mordants in question are the double plumbate of potash and lime, the double plumbate of soda and lime, and the subacetate of lead. By the employment of any one of these mordants and sulphuret of calcium, the following results are obtained:—1st, a slate-gray colour, composed solely of sulphuret of lead; 2nd, a fast black dye, having sulphuret of lead for its base; 3rd, a yellow, having for its base chromate of lead. This has been produced before in the art of dyeing, but the mordant employed for that purpose is less economical than those above mentioned.

The following is the mode of obtaining the mordants:—The subacetate of lead is formed by the combination of acetic acid with oxide of lead in excess; the double plumbate of potash and lime is formed by potassiate of lime and oxide of lead; and the double plumbate of soda and lime is formed of the sodate of lime and oxide of lead. All these products are obtained by the processes usually employed in chemistry.

Description of the Process of Dyeing.—The threads or fabrics of cotton, flax or hemp to be dyed are first to be scoured. They are then steeped in a solution of one of the above-mentioned mordants of lead, and after being taken out are allowed to drain; they are then washed with much water. In order to obtain a yellow dye, the threads or fabrics must now be passed through a solution of bichromate of potash, which produces a yellow of greater or less depth according to the shade required to be obtained.

For a slate-gray, composed solely of sulphuret of lead, the threads or fabrics, after being impregnated with the mordant, are to be dipped in a solution of sulphuret of calcium; the process is finished by softening the shade in the same manner as will be presently described for the black.

For black, the threads or fabrics, on coming from the mordant, are passed through the sulphuret of calcium; they are then washed, and converted into black by means of iron and logwood, as is generally done by the processes pursued in dyeing, which give the shade required in commerce. The dye is finally softened in the ordinary way.—Sealed June 3, 1845.

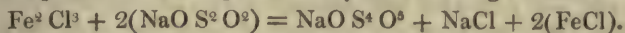
THE CHEMICAL GAZETTE.

No. LXXIX.—February 2, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Perchloride of Gold upon the Hyposulphite of Soda.
By M. J. FORDOS and A. GELIS.

IN a memoir bearing the title "On the Action of Sulphurous Acid on the Metals*," we have minutely described the chemical phenomena which occur when certain metallic solutions, capable of parting with oxygen, act upon the hyposulphites. When a solution of perchloride of iron is added to one of hyposulphite of soda, the iron is reduced to the state of protochloride, and the hyposulphurous acid is converted into a new acid, which we have called bisulphated hyposulphuric acid, as represented by the following formula :—



We have shown, in the same investigation, that the acid $\text{S}^4 \text{O}^5$ is equally formed in the reaction of salts of binoxide of copper upon the hyposulphites. The present investigation was undertaken with a view to ascertain whether the perchloride of gold acts upon the hyposulphite of soda like the perchloride of iron. Besides the scientific interest attached to this question, there is likewise one of a different kind; for it is known that the liquid at present employed to fix the Daguerreotypes is prepared by mixing aqueous solutions of perchloride of gold and hyposulphite of soda in certain proportions. The nature of this liquid is perfectly unknown, and we have thought that an accurate examination of its composition and properties would furnish the means of remedying some of the inconveniences which occur in its employment.

To obtain this liquid, the use and preparation of which have been described by M. Fizeau, 1 grm. of chloride of gold is dissolved in 500 grms. of pure water, and in another vessel 3 grms. of crystallized hyposulphite of soda in the same quantity of water. The solution of gold is then gradually poured into that of the hyposulphite, agitating the mixture the whole time; the liquid at first becomes red, but soon colourless, when the operation is finished. The question to be ascertained was, whether this liquid contained only chloride of sodium and a double hyposulphite of soda and peroxide of gold, or whether the perchloride does not rather exert in this

* *Revue Scientifique*, xiv. p. 113.

case an oxidizing action on the hyposulphite, yielding, among other products, bisulphated hyposulphate of soda, as in other analogous cases.

The liquid thus prepared is colourless, which leads to the supposition that it does not contain a persalt of gold. Admitting this supposition as proved, it is readily ascertained that the oxygen which the gold has parted with has not given rise to the production of sulphuric acid, for the precipitate which it yields with chloride of barium is soluble in hydrochloric acid. This leads us to conclude that a lower oxide of sulphur has been formed, for the liquid readily undergoes change, being decomposed even when evaporated *in vacuo*. Thus prepared, it is too dilute for analysis; and in the impossibility of concentrating it, we have been compelled to let the two salts act on one another, dissolved in very small quantities of water. The liquid thus obtained yields a very abundant precipitate with alcohol of 0.951 spec. grav. The reaction is the same as with more dilute solutions, only the mixture should be made with greater precaution; it is especially necessary to wait after each addition until the liquid is become perfectly colourless, otherwise a brown body is formed, which it is very difficult to remove, and which results from the action of the perchloride of gold on the products first formed.

Examination of the Precipitate obtained with Alcohol.—This precipitate is a mixture of several salts; it is almost entirely composed of a salt, the properties and composition of which we are about to describe, but it moreover contains variable quantities of all the products contained in the supernatant liquid. To purify it, it must be repeatedly dissolved in a little water and precipitated with absolute alcohol. The salt which we examined had been precipitated five times in this way, as long as the quantity of gold which was estimated after each precipitation varied.

The salt thus purified is perfectly colourless, and crystallizes in needles; it is insoluble in strong alcohol and but sparingly in spirit, but excessively soluble in water. It has a sweet taste. Its aqueous solution possesses all the properties of M. Fizeau's liquid; and M. Lerebour, who carefully compared the action of the two, gives the preference to the solution of our salt, on account of the richness of the tints which it imparts to the images.

This salt is the active constituent of M. Fizeau's liquid freed from all foreign substances. When heated gently in a glass tube, it gives off water, then sulphur and sulphurous acid; it consequently contains water of crystallization, which however cannot be expelled by a temperature of 212° . 1 grm. of the salt, well-dried in the air, exposed for 2 hours to 212° , lost nothing in weight; at 302° to 320° the salt became slightly yellowish, but without being perceptibly decomposed. At this temperature, 0.064, and even 0.070 of water was expelled; but this was very soon reabsorbed on exposing the salt to the air. The rapidity with which it reacquires its water of crystallization renders its estimation difficult; the salt varies in its weight each instant, and in 24 hours it has completely regained its water. When heated strongly in a platinum crucible, it leaves a

residue consisting of gold and sulphate of soda, without any trace of chloride. This property renders its analysis very easy.

When treated with nitric acid, the reaction is very lively, it disengages red vapours and deposits metallic gold; the liquid contains a large quantity of sulphuric, but no hydrochloric acid. Sulphuretted hydrogen and the alkaline sulphurets produce a yellowish-brown precipitate in its solution.

The salt contains no chlorine, but gold, sulphur and soda, the proportions of which will be seen from the following analysis:—

1. 1 grm. of salt was ignited in a platinum crucible; the residue, on treatment with water, yielded 0.374 metallic gold, and 0.407 sulphate of soda.

2. 1 grm. of salt, treated with nitric acid, gave a precipitate of 0.373 gold, and the separated liquid gave with chloride of barium 1.774 sulphate of barytes, representing 0.2433 sulphur.

These experiments, repeated several times on more than ten different samples, always gave the same results, leading to the following numbers:—

	Found.	Equivalents.	Calculated.
Gold	37.35	1	37.56
Sulphur	24.33	8	24.31
Soda	17.85	3	17.72

Supposing the sulphur to exist in the salt in the state of hyposulphurous acid and the gold as protoxide, and calculating the water by the loss, we obtain the following formula:— AuO , $\text{S}^2\text{O}^2 + 3(\text{NaO S}^2\text{O}^2) + 4\text{HO}$.

We shall now describe an experiment which shows more clearly the relations in which the gold and sulphur exist in the salt. We have already shown that the hyposulphites absorb iodine, giving rise to the new acid S^4O^2 , and that for every equivalent of hyposulphite employed half an equivalent of iodine is absorbed.

When an alcoholic solution of iodine is added to the solution of our salt, the iodine is rapidly absorbed; and if care be taken to stop the moment the liquid begins to be coloured, the quantity of iodine consumed accurately represents the amount requisite to transform the whole of the sulphur contained in the salt, supposing it to exist in it in the form of hyposulphurous acid, into bisulphated hyposulphuric acid. Subsequent examination of the liquid proved moreover that it contained bisulphated hyposulphate of soda.

I. 2 grms. of the salt absorbed 0.95 iodine from the alcoholic solution.

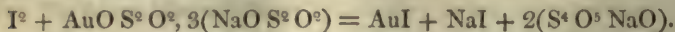
II. 1 grm. absorbed 0.485.

III. 5 grms. of iodine were dissolved in 200 cubic centimetres of alcohol, and 2 grms. of the salt required 78 divisions of Gay-Lussac's alkalimetric tube, *i. e.* 39 cubic centimetres containing 0.98 iodine.

The mean of these three experiments answers to 48.2 iodine absorbed for 100 grms. of salt; the formula requires 47.7.

This salt consequently behaves towards iodine like a hyposulphite. The gold exists in it in the state of protoxide, for when an alcoholic solution of iodine is added to a concentrated solution of the salt no

precipitate is formed; but if, after saturation with iodine, the liquid is diluted with much water, protiodide of gold is immediately deposited of a beautiful pure yellow colour; but this compound is soon converted, under the influence of the alkaline iodide in the liquid, into metallic gold and periodide. The precipitation of the protiodide of gold without any free iodine proves that it results from the double decomposition of a protosalt of gold and an alkaline iodide, a decomposition which in this case only occurs under the influence of water. The reaction of the iodine on the gold salt is represented by the following equation:—



In all the preceding experiments we have considered the salt in question as a double hyposulphite of protoxide of gold and soda; all the above experiments agree with this hypothesis; there are however others which might lead to a different supposition. Sulphate of iron, chloride of tin and oxalic acid are not capable of indicating the presence of gold in this compound. In fact, not only are the properties of this metal masked, but even some of the characters of the hyposulphurous acid. Thus nitric acid alone decomposes it in the cold: hydrochloric, dilute sulphuric and the vegetable acids may be added to its solution without producing any deposit of sulphur or disengagement of sulphurous acid. On the other hand, when chloride of barium is added to its solution, a compound is formed, which is sparingly soluble in water, but which alcohol throws down completely from the liquid as a gelatinous precipitate—a salt in which the equivalent of oxide of gold is retained, while those of the soda are replaced by barytes.

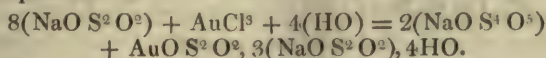
On treating this salt with an equivalent quantity of sulphuric acid, the barytes is completely separated as sulphate, and the corresponding double hyposulphite of protoxide of gold and water is obtained; this is a non-crystallizable, very acid compound, which is tolerably permanent at the ordinary temperature.

The solutions of the metals of the last sections do not yield analogous compounds; they decompose the salt entirely.

Examination of the Liquid above the Crystals.—The leys from which the preceding salt has been precipitated by alcohol, when sufficiently evaporated, yield crystals of chloride of sodium, sulphate of soda and a deposit of sulphur; there is moreover a disengagement of sulphurous acid. These different products show that, independently of the gold salt and of the chloride of sodium, there exists in these liquids a bisulphated hyposulphate of soda, which it is impossible to isolate on account of its instability. To ascertain this, we determined the quantities of the salts taking part in the reaction, in order thus to establish directly the first term of the equation which ought to represent it. We employed for this purpose a solution of gold, the strength of which was known, and added it to a known weight of hyposulphite of soda, agitating after each addition. The coloration produced by each fresh dose of perchloride of gold soon disappeared, and we stopped when the colour became permanent.

We found, on calculating our results, that each equivalent of gold employed in the state of perchloride required 8 equiv. hyposulphite of soda. To obtain accurate results, the mixture must be made slowly; otherwise it is difficult to attain the point of saturation accurately. But notwithstanding the difficulties, we consider this method as demonstrative, as we twice obtained very good results.

Each gramme of gold requires 5 grms. hyposulphite of soda, which almost exactly corresponds to the quantities prescribed by M. Fizeau in his first paper, viz. 1 gm. chloride of gold and 3 grms. hyposulphite; there must remain in the liquid a small excess of hyposulphite. It is certain however that the action of the perchloride of gold on the hyposulphite of soda may be represented by the following equation:—



There is accordingly formed bisulphated hyposulphate of soda, but this is perfectly useless in fixing the Daguerreotypes; it is indeed probably injurious, from the ease with which it parts with sulphur under the influence of heat, which may possibly contribute to the formation of those black spots which frequently cause the best proofs to be rejected; it is also probably to its presence that we must attribute in great part the alteration which M. Fizeau's liquid undergoes in the course of time; those who have made frequent use of it know that it can scarcely be kept for one month, which places the amateur under the necessity of preparing it himself; which, although simple and easy for those accustomed to chemical experiments, is by no means so for the uninitiated. To succeed, it is necessary to follow the instructions of M. Fizeau exactly, and especially to employ pure products, which it is not always easy to obtain in commerce.

We consider it therefore useful to substitute for M. Fizeau's liquid a solution of our salt; it would then suffice, to obtain a suitable liquid, to dissolve $1\frac{1}{2}$ gm. of this salt in 1000 grms. water. Another advantage is, that this salt may be readily transported; a small volume being equivalent to enormous masses of the liquid.

In this treatise we have detailed the first results obtained by acting with perchloride of gold on the hyposulphite of soda; on further action, other products are generated. Among these we have already mentioned a brown body, which is soluble in water, insoluble in alcohol, and which appears to contain more gold than the double hyposulphite we have analysed. This compound is sometimes converted into sulphuret of gold when too much of the chloride of gold is employed; and lastly, these two products, under the influence of a large excess of chloride, mutually destroy each other, and the liquid contains only sulphuric acid and metallic gold.—*Ann. de Chim. et de Phys.*, xiii. p. 394.

Copper in Biliary Calculi.

Bertozzi examined a number of biliary calculi, and in all those which were coloured, from the presence of the biliary colouring

matter, copper was found. Those which were white contained none of this metal, and the quantity appeared proportional to the depth of colour or the amount of biliary colouring matter present. The author was unable to detect any copper in the bile.

Heller confirms these results. He incinerated the calculi; the ash fused, forming an opaque light blue mass. It was dissolved in water acidulated with nitric acid, the solution neutralized and tested with hydrosulphuret of ammonia, ferrocyanide of potassium, ammonia, carbonate of potash and an iron plate. These tests exhibited the ordinary reactions of copper.—Heller's *Archiv*, 1845, Heft 3.

Chemical Researches on Cetraria Islandica.
By Dr. G. SCHNEIDERMAN and Dr. W. KNOP.

[Continued from page 34.]

III. *Lichestearic Acid*, the name assigned to this body on account of its occurrence and properties, by which it is nearest related to the fatty acids. In its pure state it is perfectly white, and forms a loose mass consisting of minute crystalline laminae possessing a mother-of-pearl lustre. It has no odour, but a peculiar rancid, acrid taste, decidedly not bitter. It is entirely insoluble in water, is dissolved by spirit in considerable quantity, and with the assistance of heat even by a very dilute spirit, from which it then crystallizes on cooling in small oblique four-sided prisms almost wholly, or when more highly concentrated, it separates partially in oily drops. When it separates from strong alcohol and by slow evaporation, it forms aggregated spheres of crystals, which resemble those of the ammonio-phosphate of magnesia under the microscope. The acid is precipitated from the alcoholic solution in white flakes by the addition of water. It dissolves readily in æther, essential and fatty oils; at about 254° it melts to a transparent, generally faintly-yellowish liquid, which on cooling again congeals to a crystalline mass without any loss of weight. It cannot be volatilized without decomposition. Lichestearic acid contains no nitrogen. The analyses were made with the melted acid, and the employment of oxygen gas, and yielded—

	I.	II.	III.			
Carbon	70.42	70.44	70.47	29 =	2178.48	70.49
Hydrogen ..	10.06	10.10	10.07	25	312.00	10.10
Oxygen	19.52	19.46	19.46	6	600.00	19.41
					3090.48	100.00

Lichestearates.—Lichestearic acid is dissolved most readily by the alkalis; the solutions undergo no perceptible change by exposure to the air, and the acid is again precipitated in white flakes on the addition of an acid. All the solutions are colourless, and possess the property of frothing considerably when boiled. In the same way as lichestearic acid has much in common with the fatty acids, so do its salts resemble in their behaviour the soaps.

Lichestearate of Potash.—When the acid is dissolved in solution

of carbonate of potash, and the solution highly concentrated by evaporation, the potash salt separates in yellowish shiny flakes, which dissolve readily in pure water, but are insoluble in the concentrated alkaline liquid. When the mass, after being perfectly dried in the water-bath, is exhausted with absolute alcohol and filtered hot, a portion of the salt separates from the filtered solution on cooling in the form of a white indistinctly-crystalline powder, which is soon converted on exposure to the air into a transparent cohesive mass, evidently from the absorption of moisture. On distilling off the alcohol, the greater portion of the salt is obtained as a syrupy mass, which dissolves readily in water. The solution has a soapy disagreeable taste, and presents a very faint alkaline reaction. On adding neutral nitrate of silver to it, we obtain the

Silver Salt, which forms a grayish-white precipitate, gradually becoming of a violet colour by exposure to light, and which softens and cakes together on boiling with water; preserved from light, and washed as quickly as possible, and dried over sulphuric acid, it forms a grayish mass, which is entirely decomposed even at a temperature of 212° , becoming brown and diffusing a rancid odour. The analysis of the salt, dried at the ordinary temperature, gave 31.84 per cent. oxide of silver; the calculation, according to the formula $\text{AgO} + \text{C}^{29} \text{H}^{24} \text{O}^5$, requires 32.77.

Lichestearate of Soda.—When a solution of the acid in solution carbonate of soda is evaporated, and the dry mass extracted with absolute alcohol and filtered hot, a colourless liquid is obtained, from which no salt is deposited even when the greater portion of the alcohol is distilled off. On mixing the residue with some water and further evaporation, a colourless syrup is obtained, from which, on long standing, a portion of the salt subsides as a white granular mass. It has a rancid acid taste, is faintly alkaline, and dissolves readily in water.

Lichestearate of Lead is obtained by precipitating the soda salt with acetate of lead; it forms a white flocculent precipitate, which cakes together when heated, and on boiling the liquid softens just like lead-plaster to a yellowish semi-fluid opaque mass, which partly rises to the surface of the liquid. When cold it forms a brittle mass, which becomes soft between the fingers and semi-fluid at 212° . It appears to undergo some decomposition even at this temperature, as it was impossible to obtain its weight perfectly constant on desiccation at 212° . The results therefore of the following analysis are only approximately correct:—

	I.	II.		
Carbon	..	49.50	29	49.82
Hydrogen	..	6.87	24	6.85
Oxygen	..	..	5	11.44
Oxide of lead.....	32.09	..	1	31.89

Lichestearate of Barytes is obtained by precipitating the soda salt with nitrate of barytes; it forms a grayish-white precipitate, which cakes together in boiling water. Its weight remains perfectly constant on desiccation in the water-bath. On analysis it yielded—

Carbon	54.95	29	55.36
Hydrogen	7.53	24	7.61
Oxygen	..	5	12.71
Oxide of barytes	24.76	1	24.32

Lichestearate of Ammonia.—Lichestearic acid forms with ammonia a crystalline compound. Solution of ammonia dissolves the acid readily with the assistance of heat; a colourless liquid is obtained, which does not become coloured on exposure to the air. On cooling, this solution becomes turbid and converted into a white gelatinous mass, which may be drawn into long threads like albumen. With the assistance of the microscope, it is readily seen that these masses consist of tissues of long, very minute crystals. On account of the mucous nature of the mass, the filtering is very slow; even after several days a thick mucus is found on the filter, to which it adheres so firmly that it cannot be separated from the paper. In the dry state it is white, silky, slightly soluble in warm water, but not to a transparent solution, as it parts with ammonia; it is readily soluble in warm ammonia.

IV. *The body C* is contained in tolerable quantity in the lichen; it requires however further examination before a name can be applied to it. It possesses very few interesting properties, is white or faintly yellowish, void of taste, insoluble in water, æther, oils, alkalies and acids, and difficultly soluble in hot spirit; the solution becomes turbid and slimy on cooling, from the greater portion again separating. The sediment presents under the microscope no distinctly crystalline appearance. The body C is destroyed by heat; on combustion it always left from 0.2 to 0.3 per cent. ash; two analyses, made with substance prepared at different times, yielded, after deducting the ash, in 100 parts—

	I.	II.
Carbon	69.99	67.39
Hydrogen	10.82	11.23

On ignition with soda-lime it gave 0.51 per cent. nitrogen. These numbers sufficiently show that this body requires further examination.

Lichen Starch.—When the pure lichen is treated with a large quantity of concentrated muriatic acid, it deliquesces almost immediately into a homogeneous mucus, which after sufficient dilution with water may be separated by a woollen cloth from the residuary lichen; the liquid which passed through could not be filtered, and was therefore divided into two parts, to both of which alcohol was added until they began to be turbid; 1 portion was then precipitated with about one-third of its volume of alcohol, which caused white flakes to coagulate in considerable quantity; upon this the precipitated liquid was mixed with the first portion and well-agitated; the mixture was now poured on to an expanded woollen cloth, through which a liquid quickly passed, having the colour and transparency of white of egg, which was precipitated by alcohol in dazzling white flakes. These, collected on a hair-sieve, dry to a colourless almost transparent mass, which does not differ in any respect in its

chemical properties from ordinary boiled and dried starch ; if, on the contrary, the muriatic extract be immediately precipitated with alcohol, and the precipitated mass, after sufficient washing, be boiled with dilute spirit, a substance may be separated by filtration, which is not coloured blue by iodine, and which possesses the properties ascribed by Mulder to lichen starch.—*Ann. der Chem.*, lv. p. 144.

Transparency of Quicksilver.

M. Melsens has found that quicksilver in minute globules is transparent, and transmits a blue light slightly tinged with violet. These globules are formed when a fine stream of water is dropped on a mercury-bath ; the drops of water, in consequence of falling with some force, become covered with a thin pellicle of mercury, which present the fact here stated. The result has been verified by Arago.—*L'Institut*, No. 605, p. 279.

Note on Iridescent Silver. By Prof. JOHN BROCKELSBY.

It is well known to those who are conversant with optical phenomena, that the brilliant play of prismatic colours exhibited by mother-of-pearl is due to the structure of the surface, provided the shell is cut and polished in a particular manner. This interesting fact was announced to the scientific world in 1829 by the discoverer, Dr. Brewster, who successfully transferred by pressure the splendid tints of the pearl to black wax, fusible metal, balsam of tolu, lead, tin, and various other substances. The colours displayed by fusible metal possess at first extraordinary beauty, which in a short time is partially lost, owing to a change that occurs upon the surface of the metal.

A few months ago, while engaged upon some experiments in electrotyping, I was led to think that by this process the hues of the pearl might be readily transferred to those metals which from their hardness are incapable of receiving impressions in mass, but yet, on account of their freedom from oxidation, retain for a long time a surface comparatively pure. I therefore took a Smee's battery, which I had just constructed, and after several experiments succeeded in obtaining small sheets of silver, radiant with the hues of the shell. When seen by a single light, as that of a lamp, the play of colours is surpassingly beautiful, scarcely inferior to that of the pearl ; and where equal care was employed, the plate of silver, which was formed eight months ago, rivals in brilliancy that which came fresh from the battery a few hours since.

The process by which this result is obtained is as follows :—The first thing required is to prepare the shell. This is effected by grinding and polishing it upon the back, in such a manner as to cut through the numerous concentric strata that compose its substance. When this is done, by the aid of a microscope the surface will be seen covered with delicate grooves, some thousands in an inch, formed by the sections of the concentric laminæ, and this configu-

ration gives rise to the glowing tints of the shell. The next step is to obtain an exact impression of this surface upon some good conductor of electricity. This we are enabled to do by means of fusible metal, if proper precautions are employed in taking the impression. I pursue exactly the same method as in taking the copy of a medal. After fusing the metal, I pour it upon oiled paper, and when the air-bubbles cease to rise through the metal the oxide is skimmed from its surface with a card; and as soon as it presents the appearance of a perfect mirror, the shell is forced down upon it by a sudden pressure. When the metal has cooled, I remove it from the shell, and having ascertained the accuracy of the impression, immediately plunge it, before any change of the surface can occur, into the silver solution, thereby completing the circuit between the poles of the battery. In a few moments the surface of the metal is frosted with silver, and the configuration of the shell exactly copied. A sheet of silver, of sufficient thickness to be easily removed with a penknife, will be deposited in the course of 5 or 6 hours under favourable circumstances. The battery I have employed consists of two plates of amalgamated zinc and one of platinized silver, 6 inches by 8. The working mixture is sulphuric acid and water, the strength varying with the temperature and the amount of work to be performed. I have found a wine-glass of acid to 3 quarts of well-water, at the temperature acquired by standing a few hours in a room at 70° F., to answer very well when the surface to be plated did not exceed $1\frac{1}{2}$ square inch. The silver solution is made by dissolving cyanide of potassium in water, and adding thereto the oxide of silver. The ratio of the ingredients I am unable to state, as I have not hitherto directed my attention to this point, but have prepared the solution by trial until I obtained the desired result.

By the process above described, we can at pleasure transfer the tints of the pearl to those pure metals which will best preserve their brilliancy; and while the knowledge of this fact is interesting as a matter of science, it may perhaps be well for the artist to consider if it cannot be applied to some ornamental purpose, and the beauty of the precious metals enhanced, by teaching them to glow with the richest hues of light.—Silliman's *Journal*, Jan. 1846.

On the Combinations of Urea with Salts. By Dr. WERTHER.

The combinations of urea with the salts are merely held together by a very weak affinity, and appear to exist only with salts whose solubility in water or alcohol does not differ much from that of the urea. Nevertheless, however, most of the double salts formed are not decomposed by boiling, and some not even by nitric and oxalic acids.

Nitrates and Urea.

I. $\text{AgO}, \text{NO}^5 + \text{C}^2\text{H}_4\text{N}^2\text{O}^2$.—When concentrated aqueous solutions of equal equivalents of urea and nitrate of silver are mixed, either

cold, or heated to 122° , a compound immediately crystallizes in large shining rhombic prisms with oblique terminal surface. The crystals are soluble in cold or hot water, as well as in cold or hot alcohol; but if the aqueous solution be boiled for some length of time, it becomes turbid, and deposits on cooling long prismatic crystals, which on being boiled with a solution of chloride of ammonia yielded chloride of silver. The decanted liquid, when evaporated to dryness and extracted with absolute alcohol, yielded large crystals of urea; the long prisms are therefore cyanate of silver. From the liquid filtered from this salt unaltered crystals of the compound employed are reobtained on cooling, if it be sufficiently concentrated; and the author could not succeed, even by frequently-repeated boiling, in converting the whole of the oxide of silver into cyanate, as asserted by Liebig; the other product of decomposition, which could not be distinctly ascertained for the above reason, is undoubtedly nitrate of ammonia. When the salt is heated slowly in a test-tube, it gives off no water, fuses, and disengages at first ammoniacal and subsequently red acid vapours. On being heated quickly, it is decomposed with evolution of light, detonation, and formation of red vapours, metallic silver being left behind. If the finely-pulverized crystals are allowed to remain for 12 hours in a water-bath at 212° , they do not alter; but after 18 hours the powder caked into a moist mass, which on being heated longer became dry, but immediately moist again on cooling; this appears to indicate the formation of nitrate of ammonia. On extracting the mass with water, however, very little cyanate of silver is left on the filter, and the liquid again yields crystals of the undecomposed salt.

An excess of nitric acid produces a precipitate of nitrate of urea, but the whole of the urea is not separated. Oxalic acid only throws down oxalate of silver. An alcoholic solution of pure soda produces in the solution of the double salt a yellow precipitate, which gives off ammoniacal vapours when heated, and becomes black on boiling with water. This body appears to contain a compound of urea with silver, for when frequently boiled with water, the residue on the filter nevertheless constantly gives off ammoniacal vapours on being heated in the dry state. At all events the precipitate is a mixture of carbonated alkali, which adheres most tenaciously, and the silver compound in question; undecomposed $\text{AgO NO}^5 + \text{C}^2\text{H}^4\text{N}^2\text{O}^3$ does not appear to form part, for when the body is decomposed by muriatic acid, the filtered solution gives no signs of the presence of nitric acid. The black body obtained from the yellow one by boiling with water appears to be a product of decomposition mixed with metallic silver, for it no longer dissolves in cold nitric acid.

The analysis of the above combination yielded—

Oxide of silver ..	49.4	50.019	49.46	1	50.42
Nitric acid	..	..	} 50.45 {	1	23.48
Urea	..	..		1	26.10

II. $2(\text{AgO, NO}^5) + \text{C}^2\text{H}^4\text{N}^2\text{O}^2$.—This compound is formed by mixing 3 to 4 atoms of nitrate of silver with 1 atom of urea. On

evaporation under the air-pump, the compound $\text{AgO}, \text{NO}^5 + \text{Ur}$ separates in the first two crystallizations; but in the third, fourth and fifth, the compound $2\text{AgO}, \text{NO}^5 + \text{Ur}$; and finally pure nitrate of silver. This compound forms large shining rhombic prisms with plane terminal surface. The analysis yielded 83.00–83.67 per cent. nitrate of silver; the above formula requires 84.9 per cent.

III. $\text{CaO}, \text{NO}^5 + 3(\text{C}^2\text{H}^4\text{N}^2\text{O}^2)$.—This compound separates from an aqueous, but better from an alcoholic solution, on slow evaporation over sulphuric acid in well-formed deliquescent crystals, which have a vitreous lustre, fuse on ignition, give off first ammoniacal and then acid vapours, and on being heated quickly explode violently, leaving behind carbonate of lime. Dissolved in water and treated with an excess of oxalic acid, oxalate of lime and oxalate of urea separate, but a great deal of the latter remains dissolved in the liquid. Nitric acid produces no precipitate in the solution. On combustion it yielded 10.65–10.4 per cent. lime; the above formula requires 10.9 per cent.

IV. $\text{MgO}, \text{NO}^5 + 2(\text{C}^3\text{H}^4\text{N}^2\text{O}^2)$.—If a solution of nitrate of magnesia and urea in absolute alcohol be slowly evaporated under the air-pump, very soon large, shining, oblique, rhombic prisms, with oblique terminal surfaces, form, which are deliquescent, and melt in the water-bath at 185° to a transparent liquid, which long after cooling exhibits only an incipient crystallization at some points. The melted mass dissolved in alcohol yields the original crystals. At a higher temperature it is decomposed like the lime-compound; the residue is magnesia. This compound is not decomposed on boiling either its aqueous or alcoholic solution; when boiled for a long time with water and treated with nitrate of silver, it yields no precipitate. Nitric acid does not separate the whole of the urea even from a concentrated solution of the salt; oxalic acid, even in large excess, produces no precipitate, nor does a solution of pure potash. The analysis of the salt yielded 10.594 to 10.24 per cent. magnesia; the formula $\text{MgO}, \text{NO}^5 + 2(\text{C}^3\text{H}^4\text{N}^2\text{O}^2)$ requires 10.6 per cent.

V. $\text{NaO}, \text{NO}^5 + \text{C}^2\text{H}^4\text{N}^2\text{O}^2 + 2\text{HO}$.—On mixing very concentrated hot aqueous solutions of nitrate of soda and urea in single equivalents, a compound of the two bodies separates on cooling in long prismatic crystals, which are permanent in the air, begin to melt at 95° , but are not quite liquid even at 212° . At 284° they begin to be decomposed, and on the application of a stronger heat they behave like the compounds previously described. The salt may be boiled in water without any precipitate being subsequently occasioned by nitrate of silver. Heated to melting and then dissolved in water, it is not decomposed, but crystallizes unaltered from it; but if first deprived of its water of crystallization and then dissolved in water, at first pure nitrate of soda crystallizes on slow evaporation, and then urea. If this mixture be dissolved in a little hot water, the combination of the two bodies separates on cooling. An aqueous solution, treated with a large excess of nitric acid, yielded no precipitate, which was also the case with oxalic acid.

The analysis, which is somewhat difficult to make, from the salt exploding on being heated, yielded—

Soda	17·67	18·90	18·00	19·06	1	19·13
Water.....	11·00	10·08	...	10·90	2	11·01

The crystals become gradually opaque on exposure to the air, and part with some water.

Nitrate of potash, nitrate of barytes and strontian, mixed with urea, gradually crystallize separately from the solution; protonitrate of mercury, added to a hot solution of urea, is partially reduced to mercury; and on evaporating the filtered solution, a basic mercurial salt, containing no urea, separates. The solution in which the ammoniacal salt existed with the urea yielded some prismatic deliquescent crystals; it could not however be decided whether they contained any urea.

Combinations of Urea with Chlorides.

I. $\text{NaCl} + \text{C}^2\text{H}^4\text{N}^2\text{O}^2 + 3\text{HO}$.—From a cold saturated solution of single equivalents of chloride of sodium and urea, very shining rhombic prisms, with oblique terminal surfaces, separate on evaporation; they deliquesce in the air, melt between 140° and 160° , part with water, and on stronger heating give off ammoniacal vapours, leaving chloride of sodium. They are very readily soluble in water, are decomposed in boiling or cold absolute alcohol, a small quantity of NaCl being dissolved with the whole of the urea. But if a tolerably concentrated aqueous solution of the crystals is mixed with 10 to 12 volumes of alcohol, nothing separates even after a considerable length of time; indeed, a certain excess of nitric acid then no longer produces any precipitation. This circumstance is important in the determination of urea in urine, as this constantly contains chloride of sodium. From a concentrated aqueous solution the urea is immediately precipitated by nitric acid, with the exception of a very small quantity. Oxalic acid forms only after a long time a precipitate of oxalate of soda, and on further concentration also of oxalate of urea. When the crystallized compound of urea with chloride of sodium is melted and then boiled in water, it is not decomposed. Analysis yielded—

Chloride of sodium	42·24	42·60	43·0	42·80
Water	...	42·55	...	12·57

II. $2\text{HgCl} + \text{C}^2\text{H}^4\text{N}^2\text{O}^2$.—This compound is immediately formed when the mixture of boiling solutions of perchloride of mercury and urea is allowed to cool; it forms very flat crystals of a faint mother-of-pearl lustre, which are sparingly soluble in cold water, and are immediately decomposed on boiling. If the aqueous solution be allowed to evaporate over sulphuric acid, crystals of the perchloride of mercury are first obtained, then of the undecomposed compound, and lastly of urea. In boiling absolute alcohol they dissolve more readily; but if the solution be evaporated even at the ordinary temperature, it is partially decomposed; the crystals begin to melt at 257° , at 263° they are perfectly liquid, at 266° they solidify to a thick paste,

from which corrosive sublimate and a trace of chloride of ammonium may be extracted by absolute alcohol; on boiling the white residue with water, a small quantity of chloride of ammonium and corrosive sublimate is removed; it is converted into a yellow powder, which heated when dry does not melt, gives off ammoniacal vapours, becoming transitorily red, while a sublimate of calomel and metallic mercury is formed. The white residue behaved therefore like the chloro-amidide of mercury.

A solution of the perchloride of mercury compound is not precipitated by nitric or oxalic acid, not even when they are added in large excess. A yellow flocculent powder is precipitated from the alcoholic solution by pure potash, which, washed with water until it no longer reacts alkaline, is insoluble in water and alcohol, becomes gray on the surface by exposure to light, and then dissolves in hydrochloric acid with separation of a small quantity of a white sediment, gives off strong ammoniacal vapours, heated when dry yields a sublimate of chloride of ammonium and mercury, and leaves in the residue a very minute quantity of a solid body (chloride of potassium).

The above compound of urea with perchloride of mercury yielded, on decomposition with sulphuretted hydrogen and nitrate of silver, 60.38 per cent. mercury and 20.944 chlorine. The formula $2\text{HgCl} + \text{C}^2\text{H}^4\text{N}^2\text{O}^2$ requires 60.73 of the former and 21.24 per cent. of the latter.

The author did not succeed in obtaining crystalline compounds with urea and chloride of potassium, chloride of ammonium and chloride of barium; chloride of strontium yielded a very deliquescent compound, which on being heated gave off but very few ammoniacal vapours, so that this might readily depend upon a mere admixture of urea.

From the composition of the above compounds urea may be regarded both as CH^2 and as $\text{C}^2\text{H}^4\text{N}^2\text{O}^2$; however, the two compounds with nitrate of silver speak very much in favour of the composition $\text{C}^2\text{H}^4\text{N}^2\text{O}^2$, as otherwise, if the second silver salt were considered as $\text{AgO}, \text{NO}^5 + \text{CH}^2\text{NO}$, the first would become $2(\text{AgO}, \text{NO}^5) + 2(\text{CH}^2\text{NO})$, and the lime and the magnesia compounds would have a still more complicated composition.—*Journ. für Prakt. Chem.*, xxxv. p. 51.

On the Property of Litharge in a State of Fusion of absorbing Oxygen. By J. LEBLANC.

Pernolet had previously observed that fused litharge contained, according to the period of its production, variable quantities of a gas which it gave off on cooling. The author obtained, on collecting this gas, 50 cubic centimetres oxygen to 2 lbs. of litharge, consequently far more than could arise from any silver that might be contained in it. Litharge therefore possesses, like silver, the property of absorbing oxygen at a high temperature and again parting with it on cooling.

If the fused litharge is allowed to flow into an iron vessel and to cool slowly in it, the surface of the mass assumes a yellow and the interior generally a red colour, which Fournet, Thenard and others have ascribed to its containing minium. The author found however that the red litharge yielded no oxygen on being heated, and became yellow on rapid cooling in water; and likewise that this litharge, on being treated with nitric acid, gave no brown hyperoxide of lead, which is a sure test for the presence of minium. It appears therefore that the yellow litharge differs from the red only in its physical structure and colour.—*Journ. de Pharm.*, viii. p. 181.

On the Equivalents of some Simple Bodies. By J. PELOUZE.

The method adopted by the author is that proposed by Gay-Lussac. Pure silver is weighed off on a fine balance which will indicate accurately $\frac{1}{4}$ of a milligramme, and from 2-6 grms. of it dissolved in nitric acid in a flask with a ground stopper capable of holding 200 cubic centimetres, and the solution diluted with 100-150 grms. water, and the chlorine compound introduced. If this is solid, it is transferred directly from the balance into the flask; but if liquid, it is weighed in a small tube, sealed before the blow-pipe, then conveyed into the flask containing the silver solution, and broken in it by violent agitation. The liquid is clarified by shaking, and the precipitation continued with a very dilute solution of silver, in which the amount of silver is accurately known, until the liquid is no longer rendered turbid. In other respects the author observed the directions given by Gay-Lussac in his treatise on the analysis of alloys of silver in the moist way. With some practice the error cannot amount to more than one-half or even one-fourth of a thousandth of the silver employed. The author came to the following results, assuming the equivalent for chlorine to be 443.20, and that for silver 1349.01 :—

Equivalent of Sodium.—100000 silver were precipitated by 54158,—54125,—54139 chloride of sodium; the mean of these three experiments gives for the equivalent of sodium 287.17, and for that of chloride of sodium 730.37. The chloride of sodium had been prepared by decomposing sulphate of soda with chloride of barium and carbonate of soda by hydrochloric acid. The salt was crystallized several times, and either dried at 392° or fused, and in both cases yielded the same results.

Potassium.—The chloride of potassium was obtained by igniting chlorate of potash; it was recrystallized and dried in the same way as the chloride of sodium. The mean of three experiments yielded for the equivalent of chloride of potassium 932.50. Marignac obtained 932.34, Levöl 932.49; the equivalent of potassium is accordingly 489.30, which agrees accurately with that found by Marignac, viz. 489.14.

Nitrogen.—In the first place, crystals of chloride of ammonium were employed which had separated from an aqueous solution, but in the second case the sublimed salt. 100 parts silver were preci-

pitated by 49·556–49·517 chloride of ammonium, which gives for the equivalent of this salt 668·38, and for that of nitrogen 175·08.

Barium.—The chloride of barium was purified by several successive crystallizations, and then dried in the oil-bath at 392° , or in a glass tube just below red heat. 100 parts silver were precipitated by 96·454–96·466–96·468 chloride of barium; hence the equivalent of the latter is 1301·14; of barium, therefore 857·94–858·16.

Strontium.—The acicular crystals obtained by crystallization were dried at 392° , or at red heat over the lamp. The first crystallization generally yields too high an equivalent; on the other hand, with chloride of barium too low a one, which appears to result from a mixture of the two salts. 100 parts silver were precipitated by 73·485 and 73·471 chloride of strontium; thence the equivalent of chloride of strontium is 991·32, and that of strontium 548·02.

Silicium.—The chloride employed was perfectly transparent, and left no residue on evaporation in a glass dish. It had been kept for a long time over mercury. After precipitation by silver, the liquid was filtered and evaporated. A residue of transparent colourless gelatinous silica remained. 100000 silver were precipitated by 39432–39470 chloride of silicium; consequently the equivalent of the chloride of silicium = 531·95–532·28, and that of silicium = 88·75 and 88·94.

Phosphorus.—Perfectly dried chlorine was passed over phosphorus until the whole had dissolved; the current was then discontinued, and a great excess of very finely divided phosphorus added. The mixture represented the protochloride mixed with a very little perchloride; after some days the liquid was decanted and shaken with tin amalgam, distilled over this tin amalgam, and rectified several times. The liquid was colourless, and did not produce any turbidness in distilled water. 100 parts of silver were precipitated by 42·74 chloride of phosphorus, whence follows the equivalent of phosphorus = 400·3.

Arsenic.—The protochloride of arsenic was distilled several times to deprive it of the excess of chlorine. It was colourless, and disappeared in a large quantity of water; the boiling-point in the rectification remained constant at 274° – 275° . The mean of three experiments was 937·50 for the equivalent of arsenic.—*Comptes Rendus*, xx. p. 1047.

On the Influence of Temperature upon the Respiration of Warm-blooded Animals. By F. LETELLIER.

The author made a series of experiments on respiration with birds and mammalia at low and high temperatures. The former varied in the experiments between 23° F. and 37° , the latter between 82° and 110° . The temperature could not be raised without the animals soon dying or becoming very uneasy. It was found that at about 32° the expired carbonic acid amounted to much more than at a higher temperature, and that this relation is more strongly marked in birds

than in mammalia*. The amount of carbonic acid in one hour was in—

	Between 59°–68°.	Between 86°–104°.	At 32°.
	grms.	grms.	grms.
A greenfinch	0·250	0·129	0·325
A turtle-dove	0·684	0·366	0·974
Two mice	0·498	0·268	0·531
A guinea-pig	2·080	1·453	3·006

Comptes Rendus, xx. p. 794.

Action of Tannin upon Starch. By J. VON KALINOWSKY.

The author added a solution of pure tannin to a cold aqueous solution of starch, removed the excess of tannin by alcohol, and obtained, after desiccation *in vacuo*, a gummy tasteless mass, which swelled to a jelly in cold water and was coloured blue by iodine. Protosulphate of iron neither coloured the mass itself nor the fluid combined with it. The analysis proved that none, or but a very small quantity of tannin, was contained in the body, whether it had been treated with cold or hot alcohol. The starch moreover always exhibited the composition $C^{12}H^{10}O^{10}$, without having been acted upon by a higher temperature.—*Journ. für Prakt. Chem.*, xxxv. p. 201.

PATENTS.

Patent granted to James Napier, Hoxton, for Improvements in treating Mineral Waters to obtain Products thereof, and for separating Metals from other Matters.

THE first part of this invention relates to the treatment of mineral waters impregnated with copper and iron.

It has hitherto been the practice to precipitate the copper contained in mineral waters simply by the introduction of pieces of iron, and the water is afterwards allowed to run into large reservoirs, where the iron absorbs oxygen from the air, and a small quantity, being thus precipitated as an oxide, is collected and sold as ochre; the water is then allowed to run off. This process is attended with many disadvantages, the chief of which is the great destruction of iron, resulting from the existence of that metal originally in the water in the state of a persulphate, which salt has the property of dissolving almost all metals, so that by its reaction upon the iron used to precipitate the copper the loss is occasioned. The patentee's improvements on this process consist,—1st, in obtaining with cer-

* These results are in apparent contradiction with those obtained by Marchand (*Chem. Gaz.*, pp. 145, 160, vol. iii.); but no other result could be expected from the frogs, as they, besides being cold-blooded animals, were brought by the low temperature nearly to a state of congelation.

tainty a much larger quantity, amounting to nearly the whole of the copper held in solution, and in a purer state; 2nd, in a more economical use of the iron employed to precipitate the copper; and 3rd, in the recovery, as a valuable product, of the iron originally held in solution, as well as that used during the process of precipitating the copper.

The first improvement is effected by adding a small quantity of sulphuric acid to the waters before introducing the iron; by this means the oxide of iron formed by the galvanic action is dissolved, and thus a clean surface of iron will be always presented to the copper salt; so that the process is facilitated, the copper precipitate obtained nearly pure, and the iron, which in the ordinary process would be mixed with the precipitate, is dissolved, forming protosulphate of iron or copperas, to be afterwards obtained by evaporation.

The second improvement is effected by reducing the persulphate of iron in solution to the state of the protosulphate, before putting in the pieces of iron used for precipitating the copper: the iron in solution being thus reduced to the proto state, with the addition of a small quantity of sulphuric acid, the copper may be precipitated with the loss of little more than an equal weight of iron.

The third object, that is, the recovery of the iron as a valuable product, is attained by evaporating the waters that have been treated as above, and crystallizing and obtaining from them sulphate of iron or copperas; after crystallization the mother-liquor may be treated in the ordinary way for obtaining ochre.

The method of carrying out these improvements is as follows:—The water to be operated upon being collected in a tank, sulphuric acid is added in the proportion of about 1 lb. thereof to 50 gallons of water, and the requisite quantity of old iron is put in; in the course of a few hours the water is completely exhausted of copper, and is then drawn off with the precipitated copper through a tap or plug-hole into a filter of sponge, cloth, or other suitable material, which retains the copper; the protosulphate of iron in solution passes through the filter, and is afterwards evaporated and crystallized.

To reduce the persulphate of iron to a protosulphate, sawdust is thrown into the tank containing the water (in the proportion of 1 lb. thereof to 50 gallons of water), at the same time that the sulphuric acid and iron are added. The patentee does not confine himself to the use of sawdust, as other vegetable matters will have the same effect, as will also the soluble portion of the refuse lime from gas works.

The object of the second part of the invention is the application to metallic ores, when in a fused state, of a current of electricity, to separate therefrom the metals which they contain.

The patentee describes the following method of treating copper ores, to illustrate this part of his invention, which is applicable to ores of other metals that are capable of being held in fusion with fluxes:—A crucible or other vessel, made of an electro-conducting material (those used by the patentee have been made of

plumbago), is prepared by lining the inside all round with clay luting, except the bottom, which is left uncovered. The regulus or calcined ore (which, when sulphurets are used, should have been roasted, to drive off as much of the sulphur as possible) is introduced into the vessel with the usual fluxes, and the vessel being then placed in an ordinary air-furnace, the heat is kept up until the mass is in a state of fusion. In the meantime, the patentee prepares a common voltaic battery of copper and amalgamated zinc, charged with acidulated water (1 part sulphuric acid to 25 parts water); he attaches to the positive wire of the battery an iron rod, having an iron disc, a little smaller than the interior diameter of the crucible, riveted at right angles to its extremity; and to the negative wire of the battery he attaches an iron rod only. The iron disc is placed on the surface of the fused mass in the crucible, and the rod is kept in contact with the outside of the crucible; the fused matter now forms part of the electric circuit, and the heat being kept up, the metal is gradually reduced, and deposited at the bottom of the crucible.

The patentee says he has found, that by merely connecting, by an external good electro-conductor, the iron on the surface of the fused mass with the bottom of the crucible, an electric circuit is formed and metal is deposited; but the result is not so satisfactory as when the battery is employed.—Sealed Oct. 22, 1844.

Patent granted to James Francis Pinel, Skinner's Place, London, for certain Improvements in the Mode of treating Farinaceous Substances.

This invention consists in the preparation of all kinds of flour (but especially the fecula of potatoes) by means of acids, in order to obtain a certain gum, which may be employed as a substitute for gum-tragacanth, Senegal, and similar gums, generally used for dressing, stiffening, glazing, sizing, dyeing, printing and finishing calicoes, nets, crapes, laces, silks, papers, and all goods or fabrics of a similar kind.

The mode of manufacturing the gum is as follows:— $\frac{1}{2}$ a gallon of nitric acid and $\frac{1}{2}$ a pint of hydrochloric acid are mixed with 100 gallons of spring water, and then as much flour or fecula as will be sufficient to form a paste being added, the whole is well-worked together, and left for 2 hours to settle; after the expiration of this time, the paste is carefully removed into buckets properly prepared for allowing the water to drain off. When sufficiently drained, the paste is divided into small lumps, which are placed on shelves in a drying room, and allowed to remain until perfectly dry; the dried paste is reduced to powder and placed on shelves in a stove, the temperature of which is raised, on the first day to 100° F., on the second day to 150°, and on the third day to 190°. After this drying process the powder is allowed to cool, and is passed through a sieve; it is then placed in an oven, the heat of which is raised to from 300° to 350° F., and when thoroughly baked it will be ready for use. The operator can ascertain if the process has been cor-

rectly carried out by mixing a small quantity of the powder with some filtered water, in which it should readily dissolve without leaving any sediment.

To produce the above gum in lumps, resembling natural gum both in colour and transparency, the patentee mixes the powder, after it has gone through the stove and been sifted with as much water as will reduce it to a paste, adding 1 part of nitric acid to 400 parts of water. When well-mixed the paste is spread upon copper dishes, in layers three quarters of an inch deep, and placed in an oven heated from 240° to 300° F.; as soon as it has become sufficiently hard it is removed from the oven into the open air, and when cool is ready for use.

If the flour or fecula is gray, that is, if it has been badly prepared and adulterated or damaged, the patentee uses, instead of the hydrochloric acid, half a pint of sulphuric acid, by the agency of which the heterogeneous substances are separated from the good flour. The mode of operating is in other respects the same as before.—Sealed May 1, 1845.

Patent granted to James Murdoch, Staple Inn, Middlesex, for Improvements in Dyeing.

This invention consists in the employment of certain materials as substitutes for cream of tartar, and for the compound of cream of tartar and alum, which are ordinarily used as mordants in dyeing.

The substitute for cream of tartar is composed of muriate of soda or muriate of potash combined with nitric acid, and instead of alum sulphate of alumina is used. The mode of preparing the ingredients is as follows:—100 lbs. of sea-salt are mixed with 300 lbs. of water, and when the salt is dissolved 20 lbs. of nitric acid are introduced; and if the mordant is required to be analogous to the compound of cream of tartar and alum, 100 lbs. of sulphate of alumina are to be gradually added to the mixture, in order to avoid as much as possible the disengagement of nitric and muriatic acid gas, which would injure the quality of the mordant.

The new mordant may be used either in the dye-bath or in the mordant-bath, in the same manner as cream of tartar or cream of tartar and alum. The patentee states, that it will be advisable, as a measure of precaution, to begin the first piece with cream of tartar or cream of tartar and alum, according to the colour of the dye-bath, especially for blacks, crimsons and violets; he recommends, for these colours, the addition of 1 part cream of tartar to 3 parts of the new mordant, to prevent the colours from changing.—Sealed June 10, 1845.

THE CHEMICAL GAZETTE.

No. LXXX.—February 16, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Analysis of the Ashes of Yeast. By Prof. MITSCHERLICH.

THE author employed, for the comminution of the yeast, which cannot be done in the usual way, an apparatus similar in principle to an ordinary coffee-mill; with which, according to the position of the screw, a coarse, and finally a very fine powder, may be obtained without any loss of substance. This apparatus deserves to be especially recommended for reducing seeds to powder. Another difficulty in the examination of the ashes of yeast is, that it fuses so readily on account of the large amount of phosphoric acid it contains; in such cases, where great accuracy is required, neither Hessian, porcelain nor platinum crucibles can be employed, as the phosphoric acid is absorbed into the mass of the Hessian crucible, attacks the porcelain, and forms with the platinum vessels in the presence of charcoal phosphuret of platinum, or when the ash principally contains potash, lime and silica, siliciuret of platinum.

These and other evils are avoided by burning the ash in a glass tube in a current of oxygen on a silver tray, which is surrounded with platinum foil to prevent the silver from being oxidized in contact with the gas. At the commencement of the combustion, the glass tube being very gradually heated, carbonic acid is passed through until no further products of distillation, which are collected in a recipient, are evolved, and then oxygen. The most anterior portion of the substance takes fire as soon as the oxygen reaches it, without the slightest detonation or disturbance, which is scarcely to be avoided when carbonic acid has not been previously passed over it. The current of oxygen is arranged according to the process of combustion, which must proceed as slowly as possible. 12 grms. of yeast and as much corn may be completely burnt in this way within an hour. The residue, which is weighed after the combustion, is placed, together with the silver tray, in a flask, and dissolved in dilute nitric acid. When the carbonaceous substance is fusible, some carburet of silver is formed, which adheres to the platinum, but is readily separated from it by solution in nitric acid. If anything should remain undissolved in the nitric acid, it is separated by filtration, and digested for some time with very concentrated muriatic acid, which dissolves the biphosphate of potash when it has

been rendered insoluble by fusion. The nitric solution is then precipitated with this latter solution or with muriatic acid, filtered, evaporated to dryness in a water-bath, and the residue, to which a trace of acid has been added, again dissolved in water. The residue in this case will be sand or silica, which latter is separated from the former by boiling in a solution of potash. The yeast contains no silica. Ammonia is then added to the solution to precipitate phosphate of lime, magnesia, iron and alumina; the two latter are not dissolved by acetic acid, with which the precipitate is digested*. The lime is thrown down from the solution by oxalic acid and the magnesia by ammonia in the state of double phosphate. Neither phosphate of lime nor phosphate of barytes are precipitated entirely by ammonia; it is therefore always requisite to precipitate the dissolved lime with oxalic acid. Moreover, the phosphate of lime sometimes dissolves entirely in acetic acid, at other times not, which depends on the formation of a crystalline phosphate of lime, which is insoluble in acetic acid. This compound is very readily obtained by dissolving phosphate of lime in muriatic acid, precipitating it with ammonia, and redissolving the precipitate in concentrated acetic acid. If it is not completely dissolved, it is filtered quickly. On leaving the clear solution for a time undisturbed, phosphate of lime separates, especially on warming, in crystals, which are insoluble in acetic acid. The ignited phosphate of lime, for instance that from bones, is likewise not soluble in acetic acid.

The solution precipitated with ammonia is slightly supersaturated with muriatic acid, upon which a solution of perchloride of iron, the amount of iron in which is known, is added to it, and then ammonia, which causes a precipitate of basic phosphate of iron and hydrated oxide of iron; the increase in weight of the peroxide of iron is phosphoric acid. The liquid is evaporated in a porcelain dish, and heated strongly to drive off the sal-ammoniac and nitrate of ammonia; upon which the chloride of magnesium, if any has dissolved in washing the phosphate of magnesia, is converted into magnesia by oxide of mercury, according to the method described by Berzelius, and this filtered, ignited and weighed. The solution of the chlorides is evaporated, fused and weighed, then dissolved in a very little water, an excess of chloride of platinum added, the filtered liquid evaporated, alcohol poured over the residue, which is then again evaporated in the water-bath to dryness, when the greater portion of the platinum separates in a metallic state; it is then strongly heated, in order to destroy entirely the chloride of platinum. The soluble portion of this residue is considered as chloride of sodium when it dissolves in an alcoholic solution of chloride of platinum, and, heated strongly with sulphuric acid, yields a salt which is readily soluble in water, and the crystals of which effloresce on exposure to the air.

* Phosphate of iron dissolves in a liquid containing acetate of iron in solution with an intense red colour. It may be precipitated from this solution by phosphoric or any other acid, by decomposing the acetic compound.

Although, in this mode of combustion, the biphosphate is not reduced by the carbon, the requisite temperature for the combustion being produced by the burning of the carbon itself in oxygen gas, it will nevertheless be requisite to test the products of distillation for phosphoric acid, and especially for muriatic and sulphuric acids and sulphuretted hydrogen.

In the burning of seed, a larger quantity may be previously carbonized faintly, and then gradually burnt in the manner above described in separate portions, in order to obtain large quantities of ash. If a part of the carbon cannot be entirely burnt, it is advisable to dissolve the residue in acids, and to burn by itself the charcoal separated by filtration.

The yeast which the author examined according to this method, was dried in a bath of chloride of zinc at a little above 248° , at which temperature it parts with all the water it can without being decomposed. In the products of distillation, no hydrochloric acid, sulphuretted hydrogen, sulphuric acid, &c. occurred. The acid in the ashes of the yeast was phosphoric acid, combined solely with lime, magnesia and potash, no iron and no alumina. Fresh top yeast, from German pressed yeast, left on burning 7.65 per cent., which consisted, in 100 parts, of 41.8 PO^5 , 39.5 KO, 16.8 2MgO , PO^5 , 2.32 CaO, PO^5 .

Fresh bottom yeast left on burning, in one experiment, 7.51 per cent., and in another 7.66 per cent. residue, consisting of 39.5 per cent. PO^5 , 28.3 KO, 23.6 MgO , PO^5 , and 9.7 per cent. 2CaO , PO^5 . By extracting with alcohol and water, the author frequently obtained biphosphate of potash in well-defined crystals from the yeast; and the acid reaction of the yeast and of the wash-water proceeds partially, if not wholly, from this cause.

Beer from which the top yeast had been removed yielded, on evaporation and burning the residue, 0.307 per cent. ash, and this 20.0 per cent. PO^5 , 40.08 KO, 0.5 NaO, 20.0 per cent. 2MgO , PO^5 , 2.6 per cent. 2CaO , PO^5 , 16.6 SiO^2 . A portion of the potash is undoubtedly combined in the beer with an acid which is destroyed on combustion. The soda is contained in the beer in the state of chloride of sodium, for it occurs as such in the grain in small quantity. It is interesting to find that the silica is extracted from the malt by the water.

The composition of the ashes of yeast is of peculiar importance for the determination of the essential inorganic constituents requisite for the development of a plant, because the yeast is formed in the midst of a liquid, from which it absorbs only those substances which are requisite for its development, and can only take up so much of the foreign substances as are contained in the surrounding fluid. Other plants absorb along with the water, which they vaporize, many salts which are not essential, so that the examination of their ashes cannot possibly lead to any satisfactory result.—*Journ. für Prakt. Chem.*, xxvi. p. 231.

On several new Series of Double Oxalates: By M. REES HEECE.

These salts were discovered in investigating the action of alkaline and earthy bases on the oxalates of the sesquioxides.

It is well known that the salts of lime produce but a slight precipitation of oxalate of lime in a moderately concentrated solution of the oxalates of the sesquioxides of iron and chromium, &c., and none in a very dilute solution of oxalate of chromium and potash, a salt discovered by Prof. Gregory, and in which there are 3 equiv. of oxalic acid combined with the alkaline base. A concentrated solution of the same salts gives rise to an abundant precipitate, which has been considered as oxalate of lime, but in which I found a considerable proportion of chromium. These were the facts which led me to pursue this inquiry.

The combination by means of which I have prepared the double salts which are the objects of this memoir, is an oxalate of chromium and ammonia, having the same formula as the salt of Mr. Gregory; but it is preferable to this on account of its great solubility.

A concentrated solution of this salt, mixed with its volume of chloride of strontium, barium or calcium, yields voluminous precipitates, which, separated from the mother-leys and recrystallized, have the following composition:—

Oxalate of chrome and barytes (A)	$3\text{Cr}^2\text{O}^3 + \text{Cr}^2\text{O}^3 + 3(\text{C}^2\text{O}^3\text{BaO}) + 12\text{HO}.$
Oxalate of chrome and barytes (B)	$3\text{C}^2\text{O}^3 + \text{Cr}^2\text{O}^3 + 2(\text{C}^2\text{O}^3\text{BaO}) + 18\text{HO}.$
Oxalate of chrome and strontian ...	$3\text{C}^2\text{O}^3 + \text{Cr}^2\text{O}^3 + 3(\text{C}^2\text{O}^3\text{SrO}) + 18\text{HO}.$
Oxalate of chrome and lime	$2(3\text{C}^2\text{O}^3 + \text{Cr}^2\text{O}^3) + 3(\text{C}^2\text{O}^3\text{CaO}) + 36\text{HO}.$

If oxide of iron is substituted for the oxide of chromium, we obtain the corresponding salts with an iron base, and which are represented by the following formulæ:—

Oxalate of iron and barytes	$3\text{C}^2\text{O}^3 + \text{Fe}^2\text{O}^3 + 3(\text{C}^2\text{O}^3\text{BaO}) + 7\text{HO}.$
Oxalate of iron and barytes	$3\text{C}^2\text{O}^3 + \text{Fe}^2\text{O}^3 + 3(\text{C}^2\text{O}^3\text{BaO}) + 12\text{HO}.$
Oxalate of iron and strontian	$3\text{C}^2\text{O}^3 + \text{Fe}^2\text{O}^3 + 3(\text{C}^2\text{O}^3\text{SrO}) + 18\text{HO}.$

The oxalate of iron and of lime does not crystallize.

If alumina is substituted for the oxide of chromium, we obtain similar salts, which are represented by—

Oxalate of alumina and barytes.....	$3\text{C}^2\text{O}^3 + \text{Al}^2\text{O}^3 + 3(\text{C}^2\text{O}^3\text{BaO}) + 10\text{HO}.$
Oxalate of alumina and barytes.....	$3\text{C}^2\text{O}^3 + \text{Al}^2\text{O}^3 + 3(\text{C}^2\text{O}^3\text{BaO}) + 30\text{HO}.$
Oxalate of alumina and strontian	$3\text{C}^2\text{O}^3 + \text{Al}^2\text{O}^3 + 2(\text{C}^2\text{O}^3\text{SrO}) + 18\text{HO}.$

The oxalate of alumina and lime cannot be isolated in a state of purity, on account of its insolubility.

These salts crystallize in small silky needles; those of the oxide of chromium are of a dark violet colour, those of iron of a greenish-yellow, and those of alumina of a brilliant white. They are soluble in about 30 times their weight of boiling water (excepting the salts of lime and oxide of chromium, of alumina and strontia, which are decomposed by water); they are scarcely soluble in cold. All the alkalis decompose them by precipitating the sesquioxide and earthy oxalate. The salts of chromium however behave differently towards ammonia, which does not throw down the oxide of chromium, even when the barytes has been separated by sulphuric acid.

The iron salts are decomposed by the solar rays, with an abundant disengagement of carbonic acid, even when the crystals are dry.

I shall conclude this summary of my investigations by drawing attention to the importance of these salts in analysis; the more so as it was with this view I undertook them.

I think that I have succeeded in explaining the fact, long since known, of the solubility of the oxalate of lime in solutions of the sesquioxides. Iron, aluminum and chromium are always separated from their ores as sesquioxides; lime and strontia, in the state of oxalates; but we know that lime cannot be separated from the solution of the sesquioxide; this circumstance is owing to the formation of a double salt, of which the oxalate of lime forms a part. It is consequently necessary to precipitate the sesquioxide by ammonia, which leaves the lime free in the solution, and it is therefore difficult to prevent its being thrown down by the carbonic acid of the atmosphere, and thus affecting the weight of the sesquioxide.

It is especially in the case of alumina and oxide of chromium, that the error may be greatest. This difficulty is easily avoided by the following process:—I will select as an instance a mineral containing iron and lime. It is dissolved in hydrochloric acid; then a suitable quantity of oxalic acid added, which, if the liquor is diluted, will not produce any precipitate: I now add some oxalate of ammonia in excess, which will precipitate the whole of the lime, which is separated by filtration, oxide of iron remaining in solution entirely free from lime; this is precipitated, in the ordinary way, by ammonia.—*Comptes Rendus*, Nov. 17, 1845.

Preparation of Chloro-acetic Acid.

M. Malaguti recommends the following process for the preparation of chloro-acetic acid readily and in large quantity:—Let chlorine act upon sulphuric æther, by which sesquichloride of carbon is obtained, and then the water which is suffered to remain in the bottles with the rough product is merely a solution of chloro-acetic and hydrochloric acids; or perchloric æther is prepared, and by distilling it and causing the product of the distillation to mix with water, a solution of chloro-acetic and hydrochloric acids is obtained. In both cases it is sufficient to employ a vacuum with sulphuric acid and potash to obtain chloro-acetic acid in a state of great purity. This process possesses the advantage of also obtaining as a secondary product a considerable quantity of sesquichloride of carbon.—*Ann. de Ch. et de Phys.*, Jan. 1846.

On the Extractive Matters of the Blood. By Dr. C. LUDWIG.

In some experiments on the transmission of organic substances from the blood into the urine, I found in the extractives of the blood a peculiar modification of the binoxide of proteine, which Mulder has shown to exist in the buffy coat*, but which had been previously

* Chem. Gaz., vol. ii. p. 113.

discovered by Scherer and V. Laer in other parts of the human body. This substance, next to the salts, constitutes the greater part of the so-called extractives of the blood, and forms an isomeric modification of the binoxide of proteine, with which we are already acquainted.

To obtain the binoxide of proteine from healthy blood, freshly drawn, beaten and strained blood is heated in an earthenware vessel over an open fire, being constantly stirred; as soon as the mass has acquired a brownish-red colour throughout, it is removed from the fire and pressed between the folds of a linen cloth. The red alkaline fluid thus obtained is treated with very dilute muriatic acid until all alkaline reaction is neutralized and the carbonates are decomposed. The neutral fluid is then rapidly heated over an open fire to ebullition; the liquid, which is either colourless or light brown when in mass, is filtered from the coagulum. Care must be taken, in the first coagulation, not to continue the heat too long, otherwise the albumen in the pressed liquid forms so dilute a solution, that on the second coagulation it falls in extremely small flakes, which pass through the filter. The least excess of acid in neutralizing the carbonates must be avoided; otherwise a small portion of the albumen is retained in solution, and would become converted into binoxide of proteine by the muriatic acid. The fluid may be known to be perfectly neutral by not becoming red or turbid on again heating, and not yielding any precipitate on the addition of a few drops of solution of carbonate of soda.

The liquid thus freed from albumen is treated with 4 or 5 vols. of alcohol of 0.848 spec. grav., which produce a slight troubling. The mixture is set aside; a layer of small white flakes subsides, which must be purified by decantation with water, æther and alcohol. If they are dense, they may be washed at once with cold water; but if very light, they should be previously treated with alcohol and æther, dried in a water-bath, and then exhausted with water.

Water removes chloride of sodium, a little phosphate of soda, and a white amorphous substance, which after drying resembles binoxide of proteine, but is obtained in so small a quantity that no elementary analysis could be made of it. Boiling alcohol removes fat and a small quantity of an amorphous substance; lastly, æther removes a considerable quantity of a beautifully-crystalline fat*.

The white substance, thus purified, is altered in colour on drying, in the peculiar manner described by Mulder, becoming brownish in places, especially on the surface. This change of colour does not depend upon decomposition, as is proved by elementary analysis, and the powder of both the white and brown mass being yellow, so that its cause probably lies in the arrangement of the molecules during drying.

This substance was dried at 212° for analysis; at a higher temperature it is decomposed, and becomes brown. It yielded—

* The presence of this fat in the aqueous extractive of blood requires further examination, as, in my opinion, it undoubtedly proves the existence of the blood-soaps, which has been lately denied.

	I.	II.	III.			
			a.	b.	c.	Scherer.
Carbon	53·61	53·77	53·78	53·52	..	53·52
Hydrogen	7·27	7·68	7·84	7·22	..	7·17
Nitrogen	..	..	..	..	14·52	14·80
Oxygen	..	..	..	..	..	24·51

No sulphur could be detected by continued ebullition with nitric acid and precipitation with chloride of barium; the precipitate formed was readily dissolved by hot muriatic acid. The above numbers agree closely with those obtained by Mulder and Scherer in their analyses of the binoxide of proteine.

A modification of this substance, which is soluble in alcohol, also occurs in the blood. Thus, if the alcohol be distilled off the liquid from which the binoxide of proteine has subsided and the residue be evaporated in a water-bath, brown flakes are deposited, which have now become insoluble in water and alcohol, and have the appearance of binoxide of proteine. Analysis confirms this view. A quantity was obtained from the blood of oxen and calves, treated with water, alcohol and æther, and dried at 248° F. It yielded, in 100 parts—

	a.	b.
Carbon	53·74	53·57
Hydrogen	7·16	7·14

a was burnt with oxide of copper only, and *b* with the addition of some chlorate of potash. In obtaining this substance, especial care must be taken previously to separate the colouring matter of the blood as much as possible from the extract. A portion, which contained some colouring matter, yielded 54·11 and 54·03 per cent. carbon and 7·50 and 7·30 per cent. hydrogen.

The whole of the binoxide of proteine is not rendered insoluble even on evaporating the alcoholic extract, for the water with which it has been washed yields a considerable quantity of a substance which exhibits all the reactions of binoxide of proteine.

The reactions of the modification of the binoxide of proteine obtained from the blood agree in most points with that obtained by Mulder and V. Laer. It differs by being soluble in water and partly in alcohol, whilst Mulder's was completely insoluble; it passes into the insoluble modification however on evaporation and precipitation with alcohol. The longer the substance has remained in the solid state, the greater is the resistance which it offers to solvents; thus when recently precipitated by alcohol, it readily dissolves in dilute solution of potash; but if it has remained in alcohol for any time, or been once dried, it does not dissolve in cold concentrated solution of potash, even by 4–5 days' exposure to its action.

A few experiments moreover showed that this substance, after having been removed from its solution, is not readily altered by external influences. If the aqueous extract of the blood be evaporated, a brown scum rises to the surface, and again forms after removal; this has been considered by many chemists as caseine; but after exhaustion with water, alcohol and æther, it possesses the composition

of binoxide of proteine. Obtained from healthy human blood and burnt with chromate of lead, it yielded in 100 parts—

	a.	b.
Carbon	..	52.97
Hydrogen	7.24	7.41

Finally, dried binoxide of proteine may be heated for 4–5 hours in a shallow dish, replacing the evaporated water, mere traces only being dissolved.—*Ann. der Pharm.*, Oct. 1845.

• *On some new Substances from Tobacco.* By M. BARRAL.

The juice obtained by digesting tobacco-leaves in water is strongly acid. This acidity has been attributed by Vauquelin to the presence of malic acid; but on crystallizing the syrup, either under the air-pump or at a gentle heat and exposure to the air, I obtained an acid in micaceous lamellæ, soluble in water, yielding an insoluble salt of lead and crystalline combinations with ammonia, nicotine, potash, &c.

This acid, which I shall call *nicotic*, is represented by the formula $C^3H O^3 + H O$, and its lead and silver salts by $C^3H O^3 + PbO$ and $C^3H O^3 AgO$. The great tendency which this acid has to form double salts, and all the reactions which it yields, lead to the presumption that the preceding formulæ should be doubled. It is decomposed by heat and sulphuric acid into acetic and carbonic acids.

This acid appears to stand in the same relation to metacetic acid as oxalic acid does to acetic acid.

The essence of tobacco or *nicotianine* contains nitrogen; on distillation with potash it yields nicotine. Its composition is—

Carbon	71.51
Hydrogen	8.23
Nitrogen	7.12
Oxygen	13.13

Comptes Rendus, Dec. 22.

On some new Double Haloid Salts. By M. POGGIALE.

Protochloride of Antimony and Chloride of Ammonium.—The protochloride of antimony combines with chloride of ammonium in two proportions. When protochloride of antimony is added to a solution of that salt, it dissolves readily, and only a slight turbidness, arising from the formation of some oxychloride, is perceptible. On evaporating the liquid at a gentle heat, at first beautiful rectangular prisms are obtained, and subsequently hexahedrons or hexahedral pyramids. The first are $3NH^3 HCl, SbCl^3 + 3HO$, and the latter $2NH^3 HCl, SbCl^3 + 2HO$. Both salts are colourless and transparent; they become yellow and opaque in moist air, but are very permanent in dry air, and are coloured yellow in the mother-ley when heated; they are likewise decomposed by a large quantity of water.

Protochloride of Antimony and Chloride of Potassium.—This salt is deliquescent, becomes yellow on exposure to the air, is de-

composed by water and also by heat; it forms laminar crystals, the composition of which is 3KCl , SbCl_3 . The mother-ley yields, on spontaneous evaporation, hexahedral crystals of 2KCl , SbCl_3 .

Protochloride of Antimony and Chloride of Sodium forms laminar crystals, having the composition 3NaCl , SbCl_3 .

Protochloride of Antimony and Chloride of Barium.—When the solution of the chloride of barium is very dilute, the two salts separate on cooling, the chloride of barium crystallizes in tablets, while the protochloride of antimony decomposes the water. It is therefore necessary, in order to obtain this compound, to use concentrated solutions. It is obtained in minute radiately-grouped needles, the composition of which is represented by 2BaCl , $\text{SbCl}_3 + 5\text{HO}$. The protochloride of antimony combines in the same way with chloride of strontium, chloride of calcium, and chloride of magnesium.

Protochloride of Tin and Chloride of Ammonium forms beautiful fascicular needles, which are permanent in the air, but are decomposed by water. The analysis of this salt, which had been previously obtained by Jacquelin, gave the formula 2NH_3 , SnCl , $\text{HCl} + 3\text{HO}$.

Protochloride of Tin and Chloride of Potassium is obtained by direct combination of the two salts, and crystallizes in beautiful long needles, which are isomorphous with the preceding salts. Its formula is 2KCl , $\text{SnCl} + 3\text{HO}$.

Protochloride of Tin and Chloride of Barium yields, on spontaneous evaporation, beautiful prisms, the *protochloride of tin and chloride of strontium* long needles. They are represented by the formulæ BaCl , $\text{SnCl} + 4\text{HO}$ and SrCl , $\text{SnCl} + 4\text{HO}$.

Chloride of Sodium and Magnesium consists of NaCl , $2\text{MgCl} + 2\text{HO}$.

Iodide of Silver and Ammonium.—Iodide of ammonium dissolves iodide of silver, forming with it a deliquescent double salt. It contains 2NH_3 , HI , AgI .

Iodide of Lead and Sodium crystallizes in yellow shining laminæ. It is obtained by adding a slight excess of iodide of sodium to a hot solution of iodide of lead, and placing the liquid in a warm spot. Its formula is NaI , 2PbI .

Iodide of Zinc and Sodium yields, on spontaneous evaporation, prismatic radiately-grouped needles. It is colourless, readily soluble in water and deliquescent. Its formula is NaI , ZnI .

Chloride and Iodide of Lead is obtained by dissolving iodide of lead in a solution of chloride of ammonium. On cooling, numerous yellowish crystals separate, which assume the form of needles, and consist of PbI , 2PbCl . On evaporating the mother-ley, crystals are obtained of 2NH_3 , HCl , $\text{PbI} + 2\text{HO}$, in the form of minute, silky, ramified needles; they become yellow in the air, and are decomposed by water.

Chloride and Acetate of Lead.—This is formed when chloride of lead is boiled in a porcelain dish with teracetate of lead, to which subsequently a slight addition of acetic acid is made. The solution is evaporated at a gentle heat, when colourless shining cry-

stals separate on cooling. The salt has a sweetish astringent taste, effloresces readily in the air, and melts at 180° ; it loses its water of crystallization at 228° . The salt is readily soluble in water; alcohol decomposes it, and precipitates chloride of lead. Several analyses yielded the formula $\text{PbCl}, 5\text{PbO C}^4 \text{H}^3 \text{O}^3 + 15\text{HO}$.

Iodide and Carbonate of Lead is prepared by digesting carbonate of lead with iodide of lead until the excess of iodide of lead has dissolved. This salt is yellow and insoluble in water. Its formula is $\text{PbI}, \text{PbO}, \text{CO}^2$.—*Comptes Rendus*, p. 1180.

Method of purifying Oxide of Uranium from Nickel, Cobalt and Zinc. By Prof. WÖHLER.

When the oxide of uranium, in its preparation from the pitchblende, has been so far purified as to be dissolved in carbonate of ammonia, sulphuret of ammonia is carefully and gradually mixed with the solution as long as a black precipitate falls. In this way nickel, cobalt and zinc are entirely separated, without any uranium being thrown down.—*Liebig's Annalen*, Oct. 1845.

On the Amount of Carbonic Acid, Alcohol and Extract of Malt in Burton Ale and Pale Ale. By L. HOFFMANN.

The results of this investigation are contained in the following table:—

Burton Ale.

Specific gravity = 1.0469 at 54°F .

	Weight according to calculation.	Weight according to calculation with the alcoholimetric tables.	Weight according to elementary analysis.	Amount in volume.	From the difference between the beer before and after being deprived of alcohol.
Carbonic acid	0.0389	..	..	0.2210	
Alcohol	(6.6220)	5.8830	6.6220	..	7.0
Extract of malt	14.9674	..	..	..	14.5
Water	78.3717				

Pale Ale.

Specific gravity = 1.0088 at 52° .

Carbonic acid	0.0667	..	..	0.3650	
Alcohol	(5.5700)	5.6540	5.5700	..	6.0
Extract	4.6210	..	..	..	4.5
Water	89.7423				

The amount of carbonic acid was ascertained by passing the gas evolved during ebullition of a weighed quantity of the beer into barytic water, and weighing the carbonate of barytes formed. The amount of alcohol was found by boiling the beer for some time in a

flask with a long, upright and then downwards-curved cooling tube. The distillate, consisting of strong alcohol, was submitted to elementary analysis, and the quantity of absolute alcohol calculated from the carbon found. To check this result, the specific gravity of the alcohol was taken; and, as will be seen from the table, the results agree tolerably well.—Liebig's *Annalen*, Oct. 1845.

PHARMACOLOGY.

A new Method for detecting spurious Musk-Pods.

By J. MOORE NELIGAN, M.D.

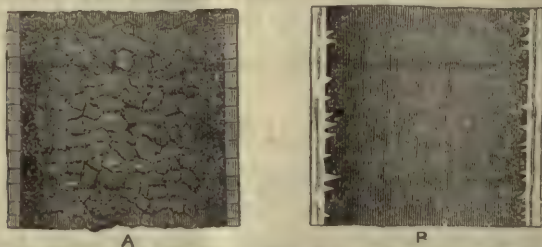
OWING to the high price and great demand for musk, both as a medicine and a perfume, it is very generally much adulterated. This fact is so well known to apothecaries and to druggists, that those who have even a moderate consumption of the drug prefer purchasing it in the unopened musk-bag, or, as it is technically called, *musk-pod*. This precaution however is often found not to be a sufficient protection against fraud, as spurious musk-pods are not uncommon in commerce, so well prepared that even the most experienced eye is often unable to distinguish the true from the false.

It is now very generally known that musk is the peculiar secretion of a small sac situated immediately in front of the preputial orifice of the male musk animal the *Moschus moschiferus*, and that it is principally imported into the British market from China. The Chinese, finding a greater demand for musk than they are able to supply with the genuine article, squeeze out some of the secretion, which is fluid in the recent state, and mix it with, it is believed, the dried blood of the animal; this compound, which presents the same physical characters as true musk, they put into small sacs made of pieces of the skin cut off from other parts of the animal's body, and prepared with the usual ingenuity of this people, so much so indeed as almost to defy detection with the naked eye.

The method hitherto adopted for detecting this sophistication has been the peculiar position of the hairs, which are arranged in a circular manner around the orifice in the genuine musk-pod, and also the absence of any remains of the penis in the artificial pods. But those characters are not invariable, and I have seen some spurious musk-pods which were so skilfully prepared as to be undistinguishable from the genuine article when compared with them.

The plan which I propose depends on the microscopic characters of the hairs which grow on the preputial sac of the musk animal, and which, as far as I have been able to detect by direct experiment, differ very remarkably from those of the false sacs which are met with in commerce. This test I have recently had an opportunity of pointing out to my friend Professor Christison of Edinburgh, and of illustrating it to him from specimens in his own museum. The

character of the hairs may be readily understood by a reference to the accompanying woodcut, of which the one marked A represents a hair from a genuine, and that marked B one from a false musk-pod. Hairs of the same size have been selected, and they are drawn as seen through a microscope of 300 diameters.



The difference appears to depend on the fact, that the hairs of this part of the animal are furnished in the interior with distinct, regular colour-cells; while in hairs taken from other parts of the animal's body those cells appear to be obliterated, as is generally the case in this and the allied tribes of animals.

The method I have now proposed is a very simple one and of easy application, and cannot be considered too scientific in the present day, when every pharmacist must be supposed to be provided with a microscope at least of the power above spoken of, without which he could not possibly detect the adulteration of arrow-root and of the other feculæ of commerce.—*From the Dublin Quarterly Journal of Medical Science.*

An easy Method of ascertaining the Genuineness of Guaiacum Wood.
By J. H. SCHWACKE.

When a few drops of a solution of perchloride of mercury are poured over some shavings of guaiacum wood in a test-tube and slightly warmed over a spirit-lamp, a bluish-green colour is immediately produced with all genuine samples. This test is easier than that by means of nitrous vapours, and is probably owing to the same cause as the blue colouring of guaiacum wood described by Schacht*. —*Archiv der Pharm.*, xlv. p. 178.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Improved Cupola for melting Iron, constructed by Messrs. Franklin Townsend and Co., Albany, New York.

THIS cupola is of the ordinary construction, only being of enlarged dimensions, and made of cast iron. Its diameter at the *tuyères*, when

* Chem. Gaz., vol. ii. p. 387.

lined with fire-brick, is 3 feet; and its height, from the hearth to the charging door, 11 feet. When charged full, it will contain 3 tons of pig iron, and is capable of melting upwards of 12 tons at one blast. The air is admitted into the cupola by six tuyères, which are placed about 15 inches above the hearth, and equidistant on the circumference of the cylinder. To avoid the number of pipes which would be necessary if the air were conducted into the cupola by the usual method, an air-chamber is made to surround the cylinder and enclose all the tuyères, and into this the main blast-pipe is introduced. An opening is made through the outside of this air-chamber, and directly opposite to each tuyère, which, being protected by a plate of glass, allows the *melter* to observe the working of the furnace. This plate of glass is so attached that it can be easily removed, and thus give free entrance to clear the tuyères whenever it may be necessary.

The air is heated by being forced through a number of small pipes, placed in such a manner in the interior of the stalk immediately above and directly over the cylinder of the cupola, that their outside surfaces are exposed to the full action of the waste heat of the furnace. For reason of the difficulty caused by the expansion of the metal when heated, these pipes are required to be of peculiar construction. By this arrangement, the air becomes heated during its passage from the blast reservoir to the tuyères upwards of 400° F.

This cupola has been in operation during the past 3 months, melting 10 tons of iron daily. The iron is *charged* in the shape of *pig and scrap* (*sprues, gates, &c.*) in about equal proportions, and is cast into stove-plates, which requires that it should be very hot and liquid. The average consumption of coal (Lehigh) in melting this quantity of iron is 225 lbs. to the ton of iron, and the rate of melting is from 2 to 3 tons per hour. An ordinary cupola, operated with cold blast, consumes upwards of 500 lbs. of coal to the ton of iron, and its rate of melting is from 1 to 2 tons per hour.

Not having the results of the operation of any hot blast cupola in this country, the comparison of the *working* of this improved cupola with them cannot be given; but its evident superiority to those of England is shown by the following extracts from a report* made by M. Dufresnoy, chief engineer of mines.

"The cupola furnaces at the 'Tyne Iron Works' are operated with heated air. The consumption of coke is 280 *livres* (309 lbs.) to the ton of iron; rate of melting, 1 ton per hour.

"At Wednesbury the cupolas are operated with hot blast, and consume 260 *livres* (287 lbs.) of coke to the ton of iron. Before the adoption of the hot blast, the consumption of coke was 400 *livres* (441 lbs.) to the ton of iron. The same quantity of iron is melted in one-half of the time that was required before the adoption of this process."—*Journal of the Franklin Institute*, Dec. 1845.

* Extrait d'un rapport de M. Dufresnoy, ingénieur en chef des mines, sur l'emploi de l'air chaud dans les usines à fer de l'Ecosse et de l'Angleterre.—Bulletin de la Société d'Encouragement pour l'Industrie Nationale, 1834, p. 299.

On a Method of forming the Dust of Graphite into a solid Mass:
By W. BROCKEDON, Esq.

The *graphite*, or black-lead of commerce, of sufficiently good quality to be used for pencils, has become very scarce, only a small quantity being now raised in the Borrodale mines, and that of inferior quality, so that what has been sold lately is part of a large supply obtained forty years ago. This quantity having been picked over and over again, the former reputation of the Cumberland graphite is now no longer sustained, and its impurity is detected by artists in consequence of the grit which it often contains.

The author of this paper has contrived a method by which the fine dust of the best parts of the graphite may be recomposed into a mass as dense and compact, and of as close a texture as the best quality found in the mine. To effect this, the dust obtained from sawing graphite into thin plates and veneers, to be enclosed in the cedar, is carefully washed and ground, and by repeated operations is rendered pure and free from grit, being finally sifted through spaces less than $\frac{1}{30000}$ th part of a square inch.

Thus prepared, the powder is placed under a powerful press on a strong die or bed of steel with air-tight fittings. The air is then pumped from the dust, and while thus free from air a plunger descends upon it, and it becomes solidified. The power employed to perform the operation is estimated at 1000 tons, several blows having been given, each of this power.

Specimens of graphite, prepared by this process from the dust of the best Cumberland black-lead, were exhibited; one of them a block in a condition to be cut into thin plates for pencils; another a broken piece, showing the same smooth surface on both sides of the line of fracture, an appearance often observed in native graphite.

The author considers it a legitimate inference to be drawn from this process, that the fine sediment deposited from the detritus of rocks may be again converted into solid stone by mere pressure.—
From the Proceedings of the Geological Society.

On the Preparation of a purified Solution of Shell-lac.
By Dr. L. ELSNER.

From time immemorial cabinet-makers have employed a spirituous solution of bleached shell-lac for coating white woods with a polish. The bleaching of the shell-lac is generally effected on a large scale by chlorine or some of its compounds; and the bleached shell-lac then costs from 2s. 6d. to 3s. per lb., while excellent orange shell-lac may be had from 10d. to 1s. If the shell-lac which has been bleached by chlorine or its compounds or by sulphurous acid, contains but a small quantity of the body employed for that purpose, it frequently happens that on polishing furniture in which there are any inlaid metallic ornaments the latter become more or less tarnished. A method therefore for purifying the solution of the yellow shell-lac, without the employment of chlorine, sulphurous acid, or any similar

substance, would have a twofold advantage; in the first place, there would not be the least fear of injuring the metal; and in the second place, it would be far less expensive than the solution of the bleached shell-lac in spirits of wine.

To attain the object in view, I turned my attention to the application of charcoal, both animal and calcined vegetable. From a series of experiments, it became evident that the animal charcoal (granulated bone-charcoal) alone was capable of yielding a practical and satisfactory result. For this purpose, equal quantities of light-coloured shell-lac were dissolved in alcohol of 0.833 spec. grav. by digestion at a gentle heat, and the two different kinds of charcoal added respectively to the solutions; the digestion was now carried on for several days, and then the solution filtered through coarse blotting-paper. The solution which had been digested with animal charcoal had a light brownish colour, was transparent and clear; maple, beech, and poplar were readily and beautifully polished by means of this solution, while that which had been digested with vegetable charcoal was of a darker colour after filtration than before. The solution of the purified shell-lac may be readily prepared on a large scale in the following simple manner:—

Any quantity of yellow shell-lac, previously broken in small pieces, is conveyed into a glass flask, alcohol of 0.833 spec. grav. poured upon it, and the whole heated on the hob, or in summer in the sun, until the shell-lac is dissolved; upon this, so much coarsely-powdered animal charcoal (it must not be too fine, otherwise on filtration particles of the charcoal pass through the filter) is added to the solution that the whole forms a thin paste. The flask is closed not quite air-tight, and left so for some time exposed to the sun; and in 8 to 14 days a small sample is filtered to ascertain whether it has acquired a light yellowish-brown colour, and whether it yields a clear, pure polish on light wood. If this is the case, it is filtered through coarse blotting-paper, for which purpose it is best to employ a tin funnel with double sides, similar to those employed in filtering spirituous solutions of soaps in the preparation of the transparent soaps, opodeldoc, &c.* The space between the two funnels is filled with hot water, and the upper aperture covered with a tin lid. By this arrangement, the spirituous solution is kept warm, and does not stop up the pores of the paper; the tin cover prevents the evaporation of the spirit. The portion which first passes may be preserved separately, and be employed as a ground or first polish. Some more spirit is poured over the charcoal on the filter, and the solution used as a last coating.

The solution of shell-lac, purified by animal charcoal, has, it is true, a brownish-yellow colour, but it is perfectly clear and transparent; when diluted with spirit, the colour is so slight that it may be used in this state for polishing perfectly white wood, such as maple, poplar and lime, without the wood acquiring the least tint of yellow. Several cabinet-makers of this town (Berlin) have employed the shell-lac polish thus prepared, and are perfectly satisfied with the re-

sults; I have also received a communication from Brunswick, stating that it has given general satisfaction.—*Journ. für Prakt. Chem.*, xxxv. p. 374.

PROCEEDINGS OF SOCIETIES.

Royal Institution.

Friday, Jan. 30, 1846.

PROF. BRANDE "On the Electro-chemical Protection of Metals."

Mr. Brande began by adverting to Sir H. Davy's electro-chemical discoveries, which formed the foundation and included the principles of all that has since been done in this extensive field of research. A principal result of Sir H. Davy's inquiries was, that the common chemical properties of the metals, and more especially their affinities for oxygen, chlorine, and bodies of that class, might be either diminished or increased by modifying their electrical states; that by placing them in what is usually termed an electro-negative condition, these affinities were lessened, whereas they were exalted by conferring upon them an electro-positive condition. In fact (said Mr. Brande), we thus arrive at such singular powers over these properties of metallic bodies in general, that we can convert many of them into what may almost be termed new or distinct metals. Thus, as regards copper plunged into nitric acid, in its ordinary condition it is rapidly oxidized and dissolved; but in its electro-negative state it resists such changes. Davy illustrated these positions by many similar instances; and as a practical application of his theoretical views, pointed out the means of protecting the copper sheathing of ships from the wear and tear occasioned by the action of seawater. He rendered the copper electro-negative by attaching to it a piece of zinc or iron, and under such influence it remained unattacked by those agents which in its normal condition induced its rapid corrosion. These researches were commenced in 1805 and 1806, and their applications were suggested in 1824 and 1825 in several papers laid before the Royal Society. Mr. Brande then proceeded to explain the meaning of the terms "electro-positive" and "electro-negative," and, by reference to diagrams and to numerous experiments, to define the directions of the electric current, with a view of preventing the misunderstanding and uncertainties which had frequently arisen on this subject. We know nothing (he observed) of the real condition of matter under the influence of electricity, nor do we know anything of the nature of electricity itself; but we are in the habit of using certain conventional terms in our reasonings and discussions upon these matters, which it is necessary accurately to define. We assume that the phenomena in question depend upon the setting up of what we call a current of electricity in certain directions; and as far as the mere passage of

this current through a conductor—a metallic wire for instance—is concerned, we call the end of the wire from which the electricity escapes the positive end, and that at which it enters the negative end; and in cases where a current of electricity is passing from one metallic surface to another, through a fluid, that surface which emits is called positive, and that which receives negative. We have two means of testing this direction of the electrical current, the one by its magnetic, the other by its chemical effects. He then proceeded to show, by the galvanometer, that the direction of the magnetic needle deviated to the east when the current of electricity was made to traverse the coil of the instrument from left to right, and to the west when the current moved in the opposite direction; and that in reference to chemical action, when two metals in communication with each other were placed in the same vessel of dilute acid, an electrical current was set up in such a direction as to pass from the metal most acted on, across the fluid, to the metal least acted on; so that the former was the positive, or generating, or active metal, the latter the negative, receiving, or passive metal—the former in all cases the *suffering*, the latter the *protected* metal. The lecturer then adduced abundance of experimental evidence upon these points. He first referred to Davy's original notion of protecting the copper sheathing of ships upon those principles, and proceeded to show by both of his tests, namely, by the galvanometer and by the chemical effects, that zinc, iron and tin were thus electro-positive in respect to copper immersed in sea-water or in acids; that those metals therefore protected the copper, which remained bright and undefiled; but that, on the other hand, platinum, gold and silver, similarly attached to copper, were electro-negative in regard to it, and that they therefore hastened its decay and corrosion. In the former case the copper was protected at the expense of the zinc, iron and tin; but in the latter the platinum, gold and silver were protected at the expense of the copper. When zinc and iron are thus employed, the zinc is the protecting, or suffering, or electro-positive metal; the iron is the protected, passive, or electro-negative metal. These points were well illustrated by the effects of dilute acid upon iron in several conditions. The iron *alone* was greatly corroded; iron with a piece of zinc attached to it remained quite bright, while the zinc was oxidized; but iron with a piece of copper attached to it was even more corroded than the simple and unprotected iron, while the copper remained bright. Mr. Brande showed that zinc and iron were of all the metals those most appropriately used as protectors, or as electro-positives, and that they thus acted in regard to the greater number of the other metals; but that, in respect to those metals themselves, the chemical affinities of zinc generally exceeded those of iron, and therefore iron might be effectually protected from all rust and decay by proper combination with zinc; but that as regarded tin and iron, the reverse was the case; and in tin-plate, no sooner is the iron abraded than its corrosion goes on with greatly increased speed. Mr. Brande showed the comparative energies of oxygen upon zinc and iron by burning those metals

in the gas; the zinc blazed with vehemence, the iron burned slowly. Copper would not, under the same circumstances, burn at all. Mr. Brande showed, in the course of his argument, that the real source of the electricity was chemical action, and not contact. With iron and copper in acid the direction of the current of electricity was from the iron to the copper; but in a sulphur solution it was from the copper to the iron, because in the latter case the copper was the metal most acted on, and therefore electro-positive.

Such is an outline of the principles insisted upon by the lecturer. He then proceeded to their practical applications, and touching upon Davy's original views in regard to copper sheathing, upon the protection of copper saucepans by tin, &c., he dwelt especially upon the extreme importance of the protection of iron by zinc in what is termed "galvanized iron." The roofing of the new Houses of Parliament, the wires of electro-telegraphs, buoys, beams and iron sheathing of ships, were especially described; and Mr. Brande said that there was scarcely any application of iron in which this admirable and simple protection was not available.—*Literary Gazette.*

PATENT.

Patent granted to Charles Joseph Hullmandel, Great Marlborough Street, Middlesex, for Improvements in producing Patterns upon Earthenware and Porcelain.

THESE improvements in producing patterns upon earthenware and porcelain, consist in obtaining a floating surface of unmingled colours (which may be drawn into any desired shape, according to the ordinary process of preparing colour for marbling paper), capable of being taken up by glazed or unglazed ware when immersed therein, and by this means producing marble patterns on such articles and combinations of various kinds of marble patterns on the same articles.

The following is one method of preparing the marbling surface :— First dissolve gum-tragacanth in water till the solution attains about the consistency of thick cream (this gum takes from 3 to 4 days to dissolve thoroughly). To this solution add water enough for it to have about 1·002 spec. grav. when weighed with an hydrometer (distilled water being 1·000 spec. grav.), or 1 part of the above solution to about 10 parts of water; and when thus thinned, add a decoction of mucilaginous matter, obtained either by boiling some flea-seeds (pulicaria or flea-wort) or a decoction of common linseed, say 1 oz. in 4 quarts of water. Of this mucilaginous decoction, put 1 part to 5 parts of the solution of gum-tragacanth above described, and mix the whole well together. Owing to the great weight of the colours used in this process, it is desirable to add to every 4 quarts of the above mixture 1 part of slip (a mixture of pipe-clay in water),

the addition of which enables the colours used for earthenware to float on the surface of the mixture, otherwise they would be apt to sink to the bottom. The solution composed of the ingredients above mentioned may be termed the "bath." The kind of colours to be employed in this part of the improved process of marbling are those known in the potteries as underglaze colours, but in addition to the usual grinding they must be reground with water on a marble slab or a thick piece of plate-glass with a muller, and kept in separate pots for use as wanted.

The trough for containing the mixture or bath is provided with a slanting board, attached to one side of the trough, and dipping into the liquid gum. The object of this board is to facilitate the cleaning of the surface of the bath, and for this purpose a wooden straight-edge is applied, so as to skim the colour left after each operation on the surface of the bath, and draw it on to the sloping board. In each of the pots containing the colours to be used, a small open brush made of hogs' bristles is placed, and to each colour a little common ox-gall is added, putting more gall gradually to each colour in the order in which it is to be used; the colour last used will therefore contain the greatest quantity of gall.

As ox-gall, in the state in which it is ordinarily used, soon putrefies, the patentee prefers to have it prepared in the following manner:—Take 1 pint of gall, and add to it 1 oz. of common salt; take another pint of gall, and add to it 1 oz. of powdered alum. Boil each mixture separately for a quarter of an hour, then mix them together. A strong sediment will remain; when cold, strain through a cloth, and put it in a bottle for use.

The bath and colours being ready for use, the colour No. 1 is splashed with a brush on to the surface of the bath; then No. 2; and so on, according to the number of colours to be employed, in the same manner as is adopted for marbling paper for bookbinders. When a good pattern, similar to the graining of marble, is produced on the surface of the bath, the porcelain or earthenware article to be ornamented is immediately dipped therein, by which means the colour floating on the top of the bath will adhere to the surface of the article so immersed. In order to obtain a good marking of the marble pattern, the earthenware must be in the state of *bisque*, not fired too hard; for the more suction the ware has, the more beautiful and clear will be the pattern. As soon as the pattern is obtained on the ware, it may, if thought desirable, be dipped into clear water, to remove the superfluous gum-water which adheres to the article. This dipping in clean water is preferred to be practised in all cases where the article has strong suction. If the article to be marbled partakes of a spherical form, like a jug or a basin, it must be rolled over the surface of the bath.

It is stated, that beautiful effects may be produced by marbling only a portion of the goods, leaving the rest blank, or ornamented by other coloured marbling, or by transferred engraving, as used already in the potteries, or by paintings by hand, appropriate to the

styles, thus combining the marbling with the various processes now in use. To obtain these effects, the parts to be protected from the marbling must be covered with a reserve, either of whitening mixed with a little gum-water, or slip and gum and sugar, or any other material already in use as reserves. If two different sorts of marbling are wanted on the same article, the part not to be marbled with No. 1 marble is covered with a reserve, and the part only which is uncovered receives the pattern. The article is then dipped in water to remove the reserve, and the ware is allowed to get quite dry; after which a reserve is placed over the part marbled with No. 1 marble, and the unprotected part is covered with No. 2 marble; the reserve is then washed off as before. By this means the ware is covered with two distinct sorts of marbles, and beautiful results, combining various coloured marbles, can be thus obtained.

When the inner surface of a basin, or other similar article, is to be marbled, a small piece of leaden pipe is bent into the shape of a siphon, and one end introduced to the interior of the article, which must be let down into the bath bottom upwards. The upper end of the pipe is jagged or pierced with holes, to allow the confined air in the basin to enter the pipe and find its way out. In effecting the marbling of the inner surface of the basin, the operator holds the pipe in one hand and the basin in the other hand; he then gradually plunges the basin into the bath (the surface of which is marbled beforehand, as above described), and gently turns the basin at the same time from right to left, or from left to right. This circular motion is to enable the marbling to adhere to the inside of the basin in a manner more agreeable to the eye. The articles marbled are, when dry, to follow the usual course of manipulations applied to earthenwares, as glazing, firing, &c.

When the process of marbling is to be used upon glazed ware, the colours are ground with oil instead of water; in this case the colours used must be those employed for "over-glaze." Previous to applying the marbling, the article to be ornamented is washed with a thin solution of resin, or of Canada balsam, or of any similar substance, in spirits of turpentine, or any similar solvent, to enable the oil colours to adhere to the glaze; on taking the ware out of the bath, it is better not to dip it in water till the colours are dry. Reserves of whitening, &c., as above explained, can be likewise employed for giving a varied marble pattern to glazed ware, as well as articles in the bisque or porous state. This over-glaze marbling can be used with great effect in conjunction with painting and batt printing, producing novel and pleasing effects.—Sealed May 22, 1845.

THE CHEMICAL GAZETTE.

No. LXXXI.—March 2, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Production of Valerianic Acid and a new Substance from Caseinē. By JUSTUS LIEBIG.

WHEN cheese prepared from fresh or sour milk, and which has been well pressed and freed as much as possible from adherent butter, is kept with an equal weight of hydrate of potash (or solution of potash, which would crystallize on cooling) in a state of fusion until hydrogen gas is evolved along with ammonia from the fusing mass, and the residue is then dissolved in hot water, slightly supersaturated with acetic acid, and the filtered solution allowed to cool, a quantity of very minute needles separate, which are very sparingly soluble in cold water and insoluble in alcohol and æther. By repeated solution in water to which some carbonate of potash is added, and precipitation with acetic acid, this body is obtained in perfectly white silky needles. From a preliminary analysis, which requires confirmation, its composition is expressed by the formula $C^{16}NH^{19}O^5$. Although readily soluble in alkalies, it combines with acids. The mother-ley from which this body crystallizes yields, on further evaporation, a considerable quantity of leucine. When the fused mass is supersaturated with tartaric acid instead of acetic acid, and the liquid submitted to distillation, an acid product is obtained, which, on saturation with barytic water, evaporation to dryness, and submitting the dry barytic salt with phosphoric acid to distillation, yields a colourless oily acid and an aqueous oily fluid possessing the odour and all the properties of valerianic acid. Leucine yields, on fusion with hydrate of potash, ammonia and hydrogen; the residue contains valerianate of potash; the formation therefore of the leucine appears to precede that of the valerianic acid when caseine is fused with potash. To within 1 equiv. of hydrogen the formula for leucine expresses the composition of an æther consisting of 1 atom cyanic acid, 1 atom oxide of amyle and 2 atoms water. By passing the vapour of the hydrate of cyanic acid into anhydrous fusel oil, a solid crystalline substance, soluble in water, is obtained, which readily crystallizes from this solvent, and in external appearance has the most striking resemblance to leucine, from which however it differs by its solubility in æther.

When the fusion is continued for a longer time, a considerable

Chem. Gaz. 1846.

quantity of butyric acid is obtained along with the valerianic acid. The silver salt, prepared with the oily valerianic acid from caseine, left on combustion 51·62 silver, so that its identity with the ordinary valerianic acid cannot be doubted. The crude distillate contains, besides valerianic acid, a volatile substance of the odour of human fæces, which reduced the nitrate of silver, but contained no formic acid; a quantity of the oxalate of potash separated from the alkaline ley previous to its being supersaturated with tartaric acid.

I have not observed, in the treatment of caseine with potash, any protide and erythroprotide, names given by Mulder to two smeary syrupy bodies, which he obtained in the action of potash upon albumen; nor do I believe that he or any other chemist has ever again obtained them of the same composition as he ascribes to them; for they are nothing more than a mixture of intermediate products, which vary according to the temperature, the duration of the action and the concentration of the alkali.—Liebig's *Annalen*, Jan. 1846.

Researches on Cinnamic Acid and Cinnamene. By E. KOPP.

The cinnamic acid employed in these researches was extracted from Peruvian balsam. For this purpose, milk of lime, sufficiently diluted with water, was made to boil, and the balsam gradually poured into it; in this way a soluble cinnamate of lime, and an insoluble resinat of lime, to which the cinnamene adheres most tenaciously, are obtained. The brownish-yellow magma is exhausted 3 or 4 times with boiling water and filtered; the solutions on cooling deposit almost white cinnamate of lime in light crystalline masses, but whose crystalline form it is impossible to determine. On being decomposed by hydrochloric acid, it yields nearly pure cinnamic acid. It may be completely purified, either by distilling it or by converting it into an ammoniacal salt, which is filtered and then decomposed by warm hydrochloric acid. The properties of cinnamic acid are already sufficiently known; it begins to boil between 572° and 579°; its density in the solid state is 1·245.

Cinnamate of Lime.—This salt is deposited from a boiling saturated solution in light masses, which have scarcely any crystalline appearance; it is very soluble in boiling water, but sparingly so in cold; it contains 2 atoms of water of crystallization, the greater portion of which is expelled at 284°. Its formula is $C^{18}H^7CaO^4 + 2aq$. The last mother-waters obtained by treating Peruvian balsam with lime, yielded a salt crystallized in hemispheres, formed of minute brilliant needles radiating from a common centre.

Cinnamate of Æthyle.—M. Plantamour found the boiling-point of this æther to be 401° (it had been prepared by the decomposition of cinnamene); Marchand found it to be 500°. I have prepared it by acting with a current of hydrochloric acid upon the mixture of 5 parts of alcohol and 3 parts of cinnamic acid; the oily liquid was distilled over oxide of lead. The density of the æther was found to be 1·126 at 32°, and its boiling-point 324°. It is therefore probable that the liquid examined by Plantamour was not cinnamic æther.

Cinnamate of Methyle is readily obtained in the same manner; its corresponding compound of alcohol. It is an oily colourless liquid, of an agreeable aromatic odour; its density was found to be 1.106, and its point of ebullition 466° .

Cinnamate of Copper.—This salt is easily obtained by mixing hot solutions of cinnamate of ammonia and sulphate of copper. It subsides immediately. When washed and dried, first in the air and then at 212° , it forms a bluish-white amorphous powder, still retaining a considerable quantity of water, the last traces of which can scarcely be removed without the salt beginning to be decomposed. When submitted to dry distillation, it changes its colour, becomes brown, and gradually diminishes in proportion as the decomposition advances. At the end of the operation, the residue exhibits on the sides of the retort the lustre of metallic copper. The volatile products consist of gas, oil, and a crystalline substance. The gas consists, at the beginning of the operation, of a mixture of carbonic acid and carbonic oxide, in the proportion of 3 to 1; towards the middle only carbonic acid is liberated, but towards the close also a small quantity of carburetted hydrogen. The oil is separated from the crystalline substance, which is pure undecomposed cinnamic acid, by means of a weak alkaline solution. The supernatant, almost colourless oil, placed in contact with chloride of calcium for a considerable length of time, and then distilled, was cinnamene $C^{16}H^8$, as was proved by its analysis and by the examination of its properties.

The products of the dry distillation of the cinnamate of copper are therefore not altogether analogous to those which are obtained with the benzoate and the salicylate of copper.

Cinnamene.—By a comparative examination of cinnamene and styrole, I am convinced that these two substances are identical; in fact, they do not differ more from one another than the different essential oils of turpentine obtained from the different turpentine of commerce.

Pure anhydrous cinnamene (it retains the last traces of humidity with great obstinacy) is a colourless, very fluid liquid, of an aromatic, highly penetrating odour, and a burning, peppery, aromatic taste. Its density, taken at 32° with the apparatus of M. Regnault, is 2.951, whilst at the temperature of 59° , it is not more than 0.928; its boiling-point is at 291° (M. Gerhardt found 284°); it refracts light strongly, and resembles in its external appearance sulphuret of carbon. It contains 2 atoms of carbon to 1 of hydrogen $C^{16}H^8$; 200 parts water were obtained for 963 parts carbonic acid; according to calculation it should have been 197. It does not solidify in a mixture of ice and salt, and dissolves perfectly in absolute alcohol, æther, the essential oils, and in sulphuret of carbon.

Poured by drops into fuming nitric acid, it dissolves with disengagement of much heat and nitrous vapours. Water precipitates a yellow resinous substance, which after washing with water possesses a very strong odour of oil of cinnamon, and irritates the eyes violently. On cautiously distilling it with water or common nitric acid, an oil is obtained which solidifies when exposed to a low tempera-

ture; the crystals, pressed between folds of blotting-paper, no longer liquify, possess a strong odour of cinnamon, irritate the eyes, and are identical with nitro-styrole. On boiling cinnamene with an excess of concentrated nitric acid, the liquid on cooling becomes filled with crystalline laminæ of nitro-benzoic acid. To convince myself of this, they were collected, saturated with ammonia, and precipitated by nitrate of silver; the silver salt, dried and distilled with precaution, yielded nitrobenzide, which is easily converted into aniline, the characters of which are very marked.

On mixing cinnamene with a tolerably concentrated solution of chromic acid, the whole solidifies almost immediately into a blackish-brown mass. On dilution with water and boiling, the chromic acid is reduced, and small white crystals of benzoic acid are obtained in the neck of the retort.

Bromide of Cinnamene, $C^{16}H^8Br$.—On mixing bromine cautiously with pure cinnamene, the whole solidifies into a crystalline mass without any disengagement of fumes of hydrobromic acid. By adding a slight excess of bromine, and exposing the yellow crystalline mass for some time to the air, it becomes white.

This body crystallizes with the greatest ease either from alcohol or from æther; on slow cooling, it is obtained in beautiful rhomboidal laminæ; but when cooled abruptly, it crystallizes confusedly in long delicate needles. It possesses a peculiar odour, which is not disagreeable, but which makes the eyes water; it fuses at 153° , and on cooling frequently remains liquid to 86° , but on the least agitation it congeals to a crystalline mass; its boiling-point is above 446° ; it may be distilled almost entirely without alteration. Treated with nitric acid, the bromide of cinnamene parts with its bromine, and yields a crystalline substance, which appears to be nitro-benzoic acid.

The bromide of cinnamene is identical with the bromide of styrole, and in my opinion the name cinnamene should be hereafter substituted for styrole, and metacinnamene for metastyrole.

I twice observed, in distilling very pure cinnamene and allowing the residuary fifth in the retort to cool, that the liquid had become so viscous that it flowed like a very thick oil on the sides of the retort; but I never witnessed a complete solidification, such as has been observed with styrole. On carrying the distillation to dryness, this thickened cinnamene yielded a further quantity of perfectly fluid cinnamene.—*Comptes Rendus*, Dec. 22, 1845.

On Gutta Percha, a peculiar variety of Caoutchouc.

By DOUGLAS MACLAGAN, M.D., F.R.S.E.

Gutta Percha is the Malayan name for a substance which is the concrete juice of a large forest tree, native of the shores of the straits of Malacca, Borneo and the adjacent countries. The tree yielding it is unknown botanically, all the information we possess regarding it being, that it is a large forest tree, and yields this product abundantly. We are indebted for our knowledge of it to Dr. W. Mont-

gomerie, H.E.I.C.S., whose spirited exertions to improve the cultivation of various articles of colonial produce at Singapore have obtained for him several distinguished marks of approbation from the Royal Society of Arts of London. For his communication regarding gutta percha, Dr. Montgomerie received a silver medal from the Society.

This substance in its crude state differs in many particulars from common caoutchouc; it is of a pale yellowish, or rather dirty white colour; it is nearly as hard as wood, though it readily receives the impression of the nail. It is very tenacious, and not at all elastic.

It seemed to me to be worth while to determine whether or not this substance really was a variety of caoutchouc, and for this purpose I subjected it to the ordinary process of ultimate analysis, and obtained as its per-centage composition,—carbon, 86.36; hydrogen, 12.15; the remainder, 1.49, was most probably oxygen absorbed from the air during the process employed for purifying it, as the substance, whilst heating on the vapour-bath, acquired a brown colour. The only analysis of common caoutchouc with which I am acquainted is that of Faraday, who obtained, carbon, 87.2; hydrogen, 12.8. The results are sufficiently near to warrant the conclusion, that the two matters in question are generically the same.

I found also that the gutta percha yields the same product of destructive distillation as the common caoutchouc. Without entering into details, I may briefly state, that both equally yield a clear yellow limpid oil, having no fixed boiling-point, and therefore being a mixture of different oleaginous principles. In both instances the distillation proceeds most freely at temperatures between 360° and 390° F., and seems almost stationary at 385°. Comparative analysis of several portions of the two oils were made, and, as is already known of common caoutchouc, the products exhibit a constitution represented by the formula $C^{10}H^8$. The gutta percha thus appears really to be a modification of caoutchouc.

In its general properties it likewise shows a similarity to common caoutchouc. It is soluble in coal naphtha, in caoutchouc oil and in æther. It is insoluble in alcohol and in water, and floats upon the latter.

Its most remarkable and distinctive peculiarity is the effect of heat upon it. When placed in water at 110°, no effect is produced upon it, except that it receives the impression of the nail more readily; but when the temperature is raised to 145° or upwards, it gradually becomes so soft and pliant as to be capable of being moulded into any form, or of being rolled out into long pieces or flat plates. When in the soft state, it possesses all the elasticity of common India-rubber, but it does not retain these properties long; it soon begins again to grow hard, and in a short time, varying according to the temperature and the size of the piece operated on, regains its original hardness and rigidity. A ball 1 inch in diameter was completely softened by boiling water in 10 minutes, and regained its hardness completely in less than half an hour. It appears to be capable of undergoing

this alternate softening and hardening any number of times without change of property.

It is also to a certain extent ductile. When soft it is easily torn across, but when hard it is very tenacious. A piece not an eighth of an inch in thickness, when cold, easily raised a weight of 42 lbs., and only broke when half a hundredweight was attached to it.

From these properties, it seems capable of many applications in the arts. Its solution appears to be as well adapted as that of common caoutchouc for making water-proof cloth; and, whilst softened, it can be made into solid articles, such as knife-handles, door-handles, &c. Malays employ it for the former of these, and prefer it to wood. A surgeon, furnished with a small piece, could easily, with the aid of a little hot water, supply himself with bougies or pessaries of any size or form.—*Edinburgh Philosophical Journal.*

On the Absence of Alkaline Carbonates in the Blood.

By JUSTUS LIEBIG.

The food of the Carnivora contains, as is well known, only alkaline phosphates, and the absence of alkaline carbonates in their blood requires no special proof; not so, however, in the Herbivora, which in their food consume a quantity of alkalies combined with vegetable acids; this being separated from the blood by the kidneys appears in the urine in the form of alkaline carbonates.

If the alkaline carbonates were essential to the constitution of their blood, if for instance the expiration of carbonic acid in the respiratory process were effected through them, they should be demonstrable as constituents of their blood. The following experiment ought to decide this question:—

If we mix 4–5 lbs. of ox-blood with 2 vols. of water, boil the mixture and subject the coagulum to strong pressure, we obtain nearly as much of an alkaline fluid as is equal to the weight of the blood. If the blood contained alkaline carbonates, they would be dissolved in this fluid. When evaporated in a retort, consequently with exclusion of air, it left about 40 cubic centimetres of a thick yellowish-brown syrup, which was very strongly alkaline, like the dilute fluid from which it was obtained. I set aside, for 24 hours, half of this concentrated fluid in a graduated tube in contact with carbonic acid gas. At the end of this time, 3 times as much gas as the volume of fluid had disappeared. If the power of the liquid to absorb 3 times its volume of carbonic acid arose from the neutral carbonate of soda it contained, and the absorption from the latter becoming converted into bicarbonate of soda; the other half of the alkaline fluid obtained from the blood, when treated with an acid, would evolve carbonic acid to the amount at least of two-thirds of the volume of the absorbed gas.

When treated with muriatic acid over mercury in a bell-glass, it mixed with it without *a trace of evolution of gas*. Hence it is evident, as Enderlin has shown in his analyses of the ashes of the

blood, that the blood of oxen really contains no perceptible quantity of alkaline carbonates.

On accurate examination, the alkaline reaction was found to arise from phosphate of soda. Urea and sugar could not be detected in the residue.—Liebig's *Annalen*, Jan. 1846.

On a new Compound of Bromine and Boron, Bromo-boracic Acid, and Bromo-borate of Ammonia. By M. POGGIALE.

The bromo-boracic acid was prepared by passing the vapours of pure bromine into a mixture of boracic acid and charcoal heated to redness. The apparatus employed consisted of a porcelain tube, to which was adapted on one side a small retort containing the bromine, and on the other a vessel furnished with the tube for collecting the gases. The mixture of charcoal and boracic acid, after being introduced into the tube, is heated at least for half an hour in order to expel any adherent moisture; the bromine is then gradually volatilized and the gas collected over mercury, which absorbs the excess of bromine.

In preparing this gas, I took all the precautions described by M. Dumas for obtaining the chloro-boracic acid, in order to avoid the formation of too large a quantity of hydrobromic acid. Thus it is requisite to change the curved tube, because it is readily obstructed by the bromide of mercury and the boracic acid, which very soon begins to deposit on the receiver. When the experiment has been made with great care, the first portions of gas contain 3 volumes of carbonic oxide and 2 volumes of bromo-boracic acid; but hydrobromic acid frequently occurs, being produced by the water contained in the corks.

I endeavoured to obtain the bromo-boracic acid by passing bromine into a glass tube containing boron and heated over a lamp; but I never succeeded in obtaining more than traces of the gas by this process, probably owing to the boron being too strongly heated. I thought I might obtain pure bromo-boracic acid by passing bromine over boride of iron, obtained by precipitating the neutral sesquisulphate of iron by borate of soda, and treating the borate of iron at a white heat with hydrogen; but the substance obtained, which was silver-white, yielded only bromide of iron. This experiment led me to examine carefully the product of the action of hydrogen on borate of iron. For this purpose I boiled it in water, and after having evaporated the solution I obtained boracic acid; the residue was pure iron. Treated with sulphuric acid diluted with half its weight of water, hydrogen was evolved, and I noticed in the liquid a white substance, which was boracic acid. These experiments appear to show that the borate of iron is decomposed by the action of hydrogen into iron and boracic acid.

Bromo-boracic acid is a colourless gas; it has a very pungent odour and a very acid taste, analogous to those of hydrochloric acid; it strongly reddens litmus-paper, extinguishes bodies in com-

bustion, and diffuses white vapours in contact with the air. It is not decomposed by heat.

This gas has the same affinity for water as chloro-boracic acid. If its solution is evaporated, a residue of boracic acid is obtained and hydrobromic acid is disengaged; thus the bromo-boracic acid decomposes water like the chloro-boracic and fluo-boracic acids.

If, after having passed some water into a test-tube full of this gas, it is agitated for a few moments, the portion which is not absorbed burns with a blue flame; but if, on the contrary, it is set light to immediately, without waiting until the white vapours are deposited or dissolved in the water, the gas is found to burn with a *green flame* having a slight bluish tint; the green colour is evidently due to the presence of boracic acid in the white vapours. This character may be advantageously employed to distinguish bromo-boracic, chloro-boracic and fluo-boracic acids—gases which diffuse white vapours in the air. When a few bubbles of dry chlorine are passed into a test-tube containing bromo-boracic acid, red vapours of bromine immediately make their appearance.

The density of the gas, determined by calculation, is equal to 8.6443. Bromo-boracic acid gives with water boracic acid and hydrobromic acid, and consists therefore of 1 vol. of boron and 3 vols. of bromine vapour:—

3 vols. of bromine	16.1799
1 vol. of boron	0.7487
2 vols. of bromo-boracic acid	16.9286
1 vol. of boracic acid	8.4643

leading to the formula BBr^3 .

The composition of bromo-boracic acid may likewise be determined by comparing the proportions of carbonic oxide and bromo-boracic acid yielded by the carbon, boracic acid and bromine, as M. Dumas did for the chloro-boracic acid.

Bromo-borate of Ammonia.—On mixing 1 vol. bromo-boracic acid with $1\frac{1}{2}$ vol. ammoniacal gas, a white, pulverulent, volatile salt, of a pungent taste, is obtained. It is soluble in water, which decomposes it into hydrobromate and borate of ammonia.—*Comptes Rendus*, Jan. 19, 1846.

On Alloxan, Alloxanic Acid, and some new Products of Decomposition of Uric Acid. By ADOLPH SCHLIEPER.

[Continued from p. 9.]

Products of Decomposition of Alloxanic Acid.—Alloxanic acid is decomposed at an elevated temperature, as is also its aqueous solution. If its aqueous solution be boiled or retained at a nearly boiling temperature, it is completely decomposed, carbonic acid being copiously evolved. If this solution be evaporated rapidly to the consistence of honey, and then treated with water, a portion only is dissolved, whilst a dazzling white crystalline powder remains behind. The dissolved portion, after having been again evaporated and

treated with water, leaves another portion of the white powder undissolved. The alloxanic acid is thus decomposed into carbonic acid and two new substances; the one which is insoluble in water is a new acid, the soluble substance is a neutral body. I propose to call the former *leucoturic acid*, the latter *difluane*.

Leucoturic Acid.—This substance constitutes the smallest part of the products of the decomposition of alloxanic acid by heat. It is obtained in the greatest quantity by rapidly evaporating a tolerably concentrated solution of alloxanic acid in a water-bath; this is best accomplished in a porcelain capsule; the clear, yellowish and gummy mass thus obtained at first froths strongly from the escape of carbonic acid; in 2–3 hours the decomposition is complete, and the mass fuses quietly; on dilution with water, it immediately becomes turbid, and the acid subsides as a white powder. 20–30 per cent. are obtained by this process. If dry crystallized alloxanic acid be carefully heated in a porcelain capsule, it fuses, puffing up violently, and on re-solution yields this substance, but in very small quantity.

Leucoturic acid forms a snow-white, granular, crystalline powder; it is insoluble in cold water, tolerably soluble in boiling water, requiring however some time; on long repose and evaporation of the hot saturated solution, it is deposited in a crystalline form. It is not acted upon by acids; nitric acid of 1·4 appeared not to alter it; this property is very characteristic. It is readily soluble in alkalies and precipitated by acids, provided the solution is recently prepared and no heat has been applied; if it be kept for some time or heated, ammonia is evolved, and it contains oxalic acid. It is soluble in ammonia with the aid of heat, and then expels carbonic acid from the carbonates of ammonia and potash. Its ammoniacal solution is unchanged by heat, and on evaporation the ammonia salt crystallizes in voluminous slender needles. The solution of the ammonia salt yields a white precipitate with nitrate of silver, which soon and spontaneously assumes a coffee-brown colour, becoming at the same time decomposed; if the precipitate be boiled, metallic silver separates without effervescence, and oxalic acid exists in the solution.

When dried at 212° and burnt with chromate of lead, it gave—

		Calculated.	Found.	
			I.	II.
Carbon	450·0	31·21	31·17	31·13
Nitrogen	354·0	24·55	24·52	24·49
Hydrogen	37·5	2·60	2·74	2·87
Oxygen	600·0	41·64	41·57	41·51
		1441·5	100·00	

Its formula is $C^6 H^3 N^2 O^6 = C^6 H^2 N^2 O^5 + H_2O$.

On combustion with oxide of copper, the nitrogen and carbonic acid were in the proportion of 1 : 3, or in 7 experiments as 325 : 1018. The volumes of nitrogen and carbonic acid in the ammonia salt were as 1 : 2. Hence, supposing the atom of water in the acid to be replaced by $NH^4 O$, the ammonia salt would be $C^6 H^6 N^3 O^6$, or

$C^6H^2N^2O^5$, NH^4 , O . Its ready decomposition by alkalis may be thus explained, $C^6H^3N^2O^6 + 3HO = 2NH^3 + 3C^2O^3$.

Diffuane.—This substance forms the largest portion of the products of decomposition of the alloxanic acid; it is readily obtained pure by evaporating the solution filtered from the leucoturic acid to the consistence of a syrup, and then treating it with great excess of absolute alcohol, which immediately precipitates the diffuane in dense white flakes. They are separated by rapid filtration, access of air being prevented as much as possible, washed with a little absolute alcohol and æther, and immediately placed *in vacuo* over sulphuric acid. After 24 hours it forms a white, light, voluminous, somewhat cohesive powder, which speedily deliquesces, forming a viscid gum. The alcoholic filtrate, which contained a considerable quantity of this substance, was slowly evaporated to drive off the alcohol; when its volume was diminished to nearly one-half, white crystalline crusts of a new substance separated in small quantity, of which I shall speak presently. The liquid filtered from the crystals was again treated with alcohol after complete evaporation, and yielded a new quantity of diffuane. Thus obtained, it forms a white loose powder, which fuses at 212° , evolving alcohol and aqueous vapour; when perfectly dried, it forms a transparent, brittle, gummy, vesiculous mass, which is easily pulverized. Its ready deliquescence is a characteristic property. It is very soluble in water; the solution does not crystallize, nor is it decomposed by boiling; it is slightly acid, of a bitter and saline taste, and yields white precipitates with salts of lead and silver. It does not combine with ammonia. It is decomposed by solution of potash even when cold, ammonia being evolved and oxalic acid being formed in the solution. When heated with nitric acid, it is decomposed with effervescence, alloxan being formed, but no alloxanic or parabanic acid. Sulphuric acid appears to exert a remarkable decomposing influence both on this substance and leucoturic acid. When a strong sulphuric solution of alloxanic acid was evaporated, it yielded a small quantity of leucoturic acid. The latter was dissolved in ammonia to purify it; but instead of at once precipitating the acid, the solution was set aside for 8–14 days, during which time it became decomposed, and oxalate of ammonia and urea were detected in it. When dried at 212° and burnt with chromate of lead, it yielded—

	Found.		Equiv.		Calculated.
	I.	II.			
Carbon	32.61	32.76	6	450.0	33.23
Hydrogen	3.94	3.85	4	50.0	3.69
Nitrogen	25.65	25.75	2	354.0	26.14
Oxygen	37.80	37.64	5	500.0	36.94
				1354.0	100.00

The carbonic acid and nitrogen were in the proportion of 3 : 1. The formation of the two above-described bodies from alloxanic acid may be thus accounted for:—

1 atom leucoturic acid	6 C	3 H	2 N	6 O
1 atom difluane	6	4	2	5
4 atoms carbonic acid	4			8
1 atom water		1		1
2 atoms of alloxanic acid	16 C	8 H	4 N	20 O

Just as alloxan is decomposed into alloxantine, parabanic and carbonic acids on boiling its aqueous solution, so is its isomeric compound, alloxanic acid, under the same circumstances resolved into leucoturic and carbonic acids and difluane.

A product was mentioned above which separated on the evaporation of the alcoholic solution after filtration from the difluane; as the quantity of this substance obtained was only 7 grms., its examination was imperfect. The proportion of the nitrogen to the carbonic acid was as 1 : 3 on the average, although there were great differences in the numbers obtained. On drying at 212°, it yielded—

	Equiv.		Calculated.	Found.
Carbon	6	450.0	35.52	35.19
Hydrogen	5	62.5	4.93	4.95
Nitrogen	2	354.0	27.95	
Oxygen	4	400.0	31.60	
		1266.5	100.00	

When speaking of procuring alloxan from uric acid and dilute nitric acid, I mentioned a remarkable new substance which I obtained once, but could not again succeed in procuring. It was obtained as follows:—

The uric acid (about 1 lb.) was oxidized by small quantities of nitric acid* of spec. grav. 1.25. 1 oz. of the uric acid was mixed with 2 oz. of the acid in a spacious dish; the solution was then cooled to 68°–86°, and poured into a large beaker-glass; after some hours it formed a thin paste of alloxan, which was separated by filtration. On dissolving the alloxan in a small quantity of hot water, a considerable quantity of uric acid was left undissolved; although the solution was almost of the density of syrup, it could not be made to crystallize; on gently heating, it became turbid and alloxantine separated. It was warmed and a little nitric acid added; considerable elevation of temperature and effervescence, from the escape of carbonic acid, immediately ensued, and on cooling the solution almost solidified from the alloxan, which was obtained pure by recrystallization.

The new substance existed in the mother-liquor filtered from the impure alloxan, which was concentrated by slow evaporation at a temperature of 104°–122°. The next morning I found the fluid, which had evaporated to two-thirds, converted into a yellow crystalline paste, which was purified by filtration and slight washing from the brown acid mother-ley; the latter contained oxalic and parabanic acids, and was not further examined; the yellow crystalline

* The nitric acid contained a little chlorine.

powder mentioned above is the acid ammonia salt of a new acid, which I shall call *hydurilic acid*. It may be readily obtained pure by dissolving the ammonia salt in about 15–20 parts of boiling water. The brown solution may be decolorized by animal charcoal, and on cooling a large number of very voluminous, dazzling white, almost microscopic needles separate, and more of them are obtained by evaporation. The acid cannot be procured directly from this salt, as it is not decomposed by acids; even when concentrated muriatic acid is boiled with it, no ammonia is removed. It was therefore decomposed by boiling with potash, and the hydurilic acid precipitated from the hot solution of the potash salt by muriatic acid.

It forms a light, loose, white powder, composed of numerous slender needles; it is nearly insoluble in cold water, more readily soluble when hot, although some time is required for perfect solution. It is insoluble in alcohol, is readily soluble in alkalis, and on the application of heat expels carbonic acid; it is also soluble in concentrated sulphuric acid without any blackening, and a small quantity only is precipitated on the addition of water. The acid forms acid and neutral salts with the alkalis; the baryta, lead and silver compounds are white precipitates, and are formed by mixing the ammonia salt with the salts of the corresponding metals. For analysis the acid was dried at 212° . The volumes of nitrogen and carbonic acid were as 1 : 4. It yielded—

Calculated.			Found.			
			I.	II.	III.	IV.
Carbon	900.0	34.70	35.59	35.60	34.58	
Hydrogen ..	62.5	2.40	2.41	2.32	2.33	
Nitrogen . . .	521.0	20.47	..	..	..	20.79
Oxygen	1100.0	42.43				
	2583.5	100.00				

corresponding to the formula $C^{12}H^5N^3O^{11} = C^{12}H^3N^3O^9 + 2HO$. The acid used in I. and II. was yellowish, that in III. was purified and snow-white.

The silver salt was obtained by decomposing the neutral ammonia salt with nitrate of silver; it formed a white precipitate, which became pale gray at 212° . It yielded—

Calculated.			Found.		
			I.	II.	III.*
Carbon	900.0	17.07	..	..	17.75
Hydrogen ..	37.5	0.71	..	..	1.03
Nitrogen	531.0	10.07			
Oxygen	900.0	17.09			
2 Oxide of silver	2903.2	55.06	54.69	54.42	
	5271.7	100.00			

corresponding to the formula $C^{12}H^3N^3O^9 + 2AgO$.

* This portion of the salt was accidentally heated to 248° for a short time, and became slightly reddish.

The solution of the acid in potash only crystallizes when completely dried, forming small warts; it is insoluble in alcohol.

Neutral hydurilate of Soda was obtained by heating the acid with a little water to ebullition, and adding carbonate of soda as long as effervescence ensued. The acid dissolved, but the soda salt almost immediately fell as a crystalline difficultly-soluble powder, the quantity of which increased on cooling. As the liquid did not contain excess of carbonate of soda, the whole of the hydurilate of soda was precipitated by alcohol. When dry it formed a heavy, white, crystalline powder; it was tolerably soluble in water. At 212° , it falls to a bulky light powder, losing water and becoming somewhat reddish.

It was analysed after drying at 212° , and yielded—

Calculated.				Found.		
				I.	II.	III.
Carbon	900.0	24.24	12	..	..	24.74
Hydrogen	100.0	2.68	8	..	..	2.59
2 Soda	781.8	21.06	2	20.77	20.76	

corresponding to $C^{12}H^3N^3O^9, 2Na + 5aq$.

Hydurilate of Ammonia is obtained by dissolving the acid ammonia salt or the acid in ammonia and evaporation in a water-bath; a little excess of ammonia however remains. On cooling, the solution crystallizes in long, flattened, silvery-white needles. It is tolerably soluble in water, very readily so when free ammonia is present. When treated with acids, the acid ammonia salt is precipitated in fine white needles. On combustion, the volumes of nitrogen and carbonic acid were as 5 : 12. It yielded—

Calculated.				Found.	
				I.	II.
Carbon	900.0	28.70	12	29.20	28.74
Hydrogen	150.0	4.78	12	5.27	5.02
Nitrogen	885.0	28.18	5	28.70	28.26
Oxygen	1200.0	38.34	12	36.83	38.08
	3135.0	100.00			

Hydurilic acid may be regarded as a compound of 3 atoms of urilic acid with 10 atoms of water, $C^{24}N^6O^{12} + 10HO = 2(C^{12}H^3N^3O^{11})$. It is evidently formed from the imperfect oxidation of uric acid.

[To be continued.]

On Binoxide of Proteine. By J. LIEBIG.

Bouchardat states, that if moist fibrine be placed in water containing $\frac{1}{2000}$ th part of muriatic acid, the fibrine speedily becomes gelatinous; by a continued action we obtain a solution which appears turbid from the presence of a small quantity of fatty matter. Bouchardat designates that portion which is soluble in dilute muriatic acid albuminose, the insoluble portion epidermose.

Mulder states* that this experiment has been repeated by Von Baumhauer. The solution of the fibrine, obtained by means of muriatic acid, in Baumhauer's experiments, was precipitated by carbonate of ammonia and exhausted with alcohol. The dried precipitate yielded on analysis—

	I.	II.
Carbon	53·64	53·65
Hydrogen	6·88	6·73
Nitrogen.....	15·88	
Oxygen	23·64	

Mulder concludes from this, "that albuminose is also a product of the oxidation of proteine, which is doubtless formed by the action of the air upon the substance produced by the agency of the muriatic acid and subsequently dissolved. It is binoxide of proteine, $C^{40}H^{31}N^{10}O^{34}$." We have lately become acquainted with so many various matters, which although essentially different in their properties, must be considered, according to the analyses, as oxides of proteine, that I was extremely anxious to convince myself of the existence of one of them. I have found that, if by binoxide of proteine we are to understand a body which contains no sulphur, the substance examined by Baumhauer cannot be classed among the oxides of proteine, since the whole of the sulphur contained in the fibrine exists unchanged in it.

I have observed that the air and the oxygen it contains exert no influence on the solution of fibrine in muriatic acid. If the moist fibrine be allowed to swell up and become gelatinous in dilute muriatic acid, and we then dilute with a large quantity of water, and filter the liquid (thus before solution ensues), the existence of lime and phosphoric acid in it can be proved. If the fluid be heated for a longer time and more strongly, so that the whole is dissolved, and a portion of this fluid be heated to ebullition with excess of potash, on neutralization with acetic acid we have copious evolution of sulphuretted hydrogen, and a drop of acetate of lead causes a black precipitate in it.

Hence, on dissolving fibrine in dilute muriatic acid of the above strength, the sulphur remains in combination with the other elements of the fibrine. If the muriatic solution of the fibrine (the albuminose of Bouchardat) be mixed with solution of chloride of sodium, sulphate of soda or nitrate of potash, it coagulates, forming a kind of caseous or albuminous mass, which can be washed with a saturated solution of chloride of sodium. The liquid which runs through, and contains the chloride of sodium, does not now contain any further perceptible trace of lime or phosphoric acid; both exist in the precipitate; nor does it contain any oxidized product of sulphur, and when boiled with solution of potash does not yield any reaction of sulphuret of potassium. The albuminose of Bouchardat is however, according to Mulder, binoxide of proteine. As such, the precipitate should not contain any phosphate of lime or sulphur; but

* Chem. Gaz., vol. ii. p. 118.

when dissolved in and boiled with solution of potash, it yields a black precipitate of sulphuret of lead on the addition of a salt of lead, and acids cause an evolution of sulphuretted hydrogen.

This substance is therefore not binoxide of proteine.—Liebig's *Annalen*, Jan. 1846.

ANALYTICAL CHEMISTRY.

On the Quantitative Estimation of Bromine in Mineral Waters.

By M. HEINE.

[THIS process is described in a work bearing the title, "Chemical Investigation of the Brines, Salts and residues of the Graduation Works in Saxony and Westphalia." Hitherto we possessed no accurate quantitative method for the determination of this important substance in mineral waters. Although the process of M. Heine cannot lay claim to the most perfect accuracy, we have no doubt it will be found preferable to any other method now in use.]

The usual qualitative test for bromine consists in mixing the solution supposed to contain the bromides with some æther, then carefully adding chlorine water and leaving the fluid in quiet; the æther collects on the surface. It is colourless when no bromine is present, faintly yellow when there is little, slightly or strongly brown when in greater quantity. To make use of this test in quantitative investigations, several precautions must be taken. In the first place, it had to be ascertained whether the mother-leys, which are sometimes of a yellow colour, would impart this colour to the æther; experiments proved this not to be the case. On adding chlorine water to the leys, they were more or less decolorized, a proof that the yellow colour was owing to organic substances. It is further known that æther assumes a faint yellow tint when it is shaken with chlorine water; it became requisite to know whether a small quantity of chlorine water is capable of producing this coloration, or only large quantities. A considerable amount of chlorine water was employed before its influence on the colour of the æther became perceptible. In order to conclude with probability as to the quantity of bromine, so much chlorine water had to be employed that all the bromine was set free and taken up by the æther. It was therefore requisite to determine this quantity by the addition of more or less chlorine water to liquids containing the same amount of bromine, and by comparing the tints of the æther*. The volatility of the æther and of the bromine had also to be considered, and the glasses had to be made so that they could be closed tight and very quickly, and at the same time be almost entirely filled. And lastly, it was requisite to use equal quantities of æther, &c. for all the experiments, and equally coloured, or rather colourless glasses of the same size, that the layer of æther might be of the same height and breadth.

* It is necessary to use the strongest possible chlorine water recently prepared.

In the next place, a series of liquids containing a known amount of bromine was prepared by dissolving in every 25 grms. of distilled water from 5 to 50 milligrms. of bromine. In this way I formed a series of equally large test-tubes of white glass, which contained in the same quantity of water (25 grms.), 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 milligrms. of bromide of potassium. Equal quantities of æther, measured in the same glass, were added to these solutions, and the tubes immediately closed.

The same vessel which served to measure the æther answered also for the chlorine water, it having been previously found by experiment that more chlorine water did not render the æther of the solution containing most bromine darker. The addition of the chlorine water to the test-glasses was likewise effected as quickly as possible. They were then well shaken; the æther soon collected on the surface, and a beautiful, extremely regular scale of colours from yellow to brown was obtained—a proof that the solutions might serve as standards for comparison. Beyond 50 the comparison becomes more uncertain, because the tints of every additional 5 milligrms. of bromide of potassium can no longer be well-distinguished on account of the dark colour. It is however evident that 5 milligrms. bromide of potassium = 3·3 milligrms. bromine, dissolved in 25 grms. water, diluted therefore 7600 times, exhibit a remarkable reaction, and that the limit of sensibility is far greater, certainly beyond 20,000 times dilution.

As soon as the scale of colours had been prepared, the glasses filled with mother-ley and æther, which were perfectly similar in size and had been previously arranged, were shaken with chlorine water, and the tints produced compared with those of the test-glasses. Each glass contained equal volumes of the ley from the different salt-works, measured in a vessel capable of containing 25 grms. of water; and the same quantities of æther and chlorine water were added to them as to the test-liquid. The operation requires to be made with great haste, because after some time the colour of the æther decreases, and entirely disappears in the course of 12 to 16 hours.

The following are the results of several experiments:—

No.	Spec. grav.	Mother-ley.	Salt-works.	Corresponded to a test-liquor containing bromide of potassium. Milligrms.	The ley consequently contains	
					Bromide potassium.	Bromine.
		Grms.			In 100 parts.	
1.	1·255	31·375	Halle	41	0·131	0·087
2.	1·270	31·750	Kösen	36	0·113	0·075
3.	1·315	32·875	..	35*	0·107	0·071
4.	1·303	32·575	Artern	32	0·098	0·065
5.	1·250	31·250	Schönebeck	29	0·093	0·062
6.	1·273	31·825	..	33	0·104	0·069

* This sample on shaking yielded a froth which floated in the layer of æther, and somewhat prevented the comparison of the colour; however, the error cannot be very considerable.

In such cases as the above, in which the amount of bromine is by no means considerable, the method proposed for ascertaining its amount by means of a scale of colours appears to me more certain than the analytical determination from the mixture of chloride and bromide of silver according to Rose. The numbers obtained for the bromine should properly be subtracted from the amounts of chlorine; but they are not sufficiently large to render a re-calculation of the results of the analysis of the leys necessary.

Quite as accurately, if not more so, may iodine be estimated in liquids by the well-known method with solution of starch and nitric acid. A large amount of chlorine (which is the case in the brines and leys from salt-works) is, it is true, a hindrance; I have however convinced myself, by the addition of $\frac{1}{3000}$ iodide of potassium, that the reaction with starch and sulphuric acid is still perceptible. I only obtained distinct evidence of iodine in the mother-leys from the salt-works of Halle; in all the others none, or so very slight, that the presence of iodine cannot be asserted positively.—*Journ. für Prakt. Chem.*, xxxvi. p. 181.

On Chloride of Platinum and Starch as Tests for Iodine.

By VON COTTEREAU.

Some time ago M. Aquilina recommended the chloride of platinum as a test for iodine and the iodides, it being coloured red by them. According to the author, however, this merely holds good with the iodides, for instance iodide of potassium; and even in this case the starch is a far more sensitive test for the liberated iodine, which of itself produces scarcely any perceptible change in the chloride of platinum. Even the acetate of lead is a superior test for iodine compounds to the chloride of platinum.—*Journ. de Chim. Méd.*, xi. p. 637.

On the Quantitative Separation of Antimony from Tin.

By Dr. L. ELSNER.

M. Levol* has proposed, for the quantitative separation of the above two metals, digesting 2 grms. of any given alloy with muriatic acid at a gentle heat, and then adding a concentrated solution of chlorate of potash until the alloy has entirely dissolved. Both the metals are then precipitated from the solution by a bar of distilled zinc, and the metallic powder boiled for an hour with muriatic acid. The residuous, black, pulverulent antimony is dried on a weighed filter and its weight ascertained; the tin is thrown down from the liquid filtered from the antimony by sulphuretted hydrogen gas.

I have repeated these statements of M. Levol, and have obtained the following results:—In the first place, the employment of 2 grms. of metallic alloy for a quantitative analysis is too much; 1 gm. is perfectly sufficient. In one instance, a mixture of $\frac{1}{2}$ gm. of tin and

* This method has been fully described at p. 62 of our third volume.—ED.

as much antimony, and in another experiment an alloy of the two metals, fused together in the above proportions, was treated, according to the statement of M. Levöl, with muriatic acid and chlorate of potash with the assistance of heat until the alloy had dissolved; it however required comparatively *a very considerable quantity* of chlorate of potash. The two metals were then precipitated from the solution by a bar of zinc as a fine black powder, collected on a filter, washed with water, and boiled in a porcelain dish with chemically pure muriatic acid, and in the second experiment digested continuously in a similar vessel on the sand-bath.

The acid liquid filtered from the black powder, on being treated with recently-prepared sulphuretted hydrogen, yielded a precipitate which evidently consisted of two differently-coloured layers; the inferior layer was clearly the orange-red precipitate of sulphuret of antimony, above which was the chocolate-brown protosulphuret of tin. It is certain therefore that some antimony had dissolved along with the tin, and that consequently this proposed method of separating the two metals has no claim to accuracy. I may observe, that the antimony employed for the experiment, as well as the tin, was free from lead; this was previously ascertained by the reactions on charcoal, as well as with sulphuric acid and chromate of potash. M. Levöl observes that M. Chaudet had previously proposed separating the two metals by treatment with muriatic acid, but that in an alloy containing more than 1 part of antimony to 20 parts of tin, an addition of tin must be previously made before the method can be applied. M. Levöl moreover observes, that when it is not an alloy, but merely a mechanical mixture of the two metals, as obtained by precipitation with zinc, on treating it according to his directions, the separation of the two metals is readily and surely accomplished under every condition.

In the two experiments above mentioned, equal parts of the two metals had been precipitated from their solution in the state of a mechanical mixture by zinc; and nevertheless the reaction with sulphuretted hydrogen proved that beside the tin, some antimony had dissolved. Laminar crystalline antimony in whole pieces, and also extremely divided black pulverulent antimony precipitated by zinc from the protochloride, on being boiled with pure muriatic acid, yielded a liquid in which sulphuretted hydrogen produced an orange-red precipitate of sulphuret of antimony. It is evident from these experiments that antimony is partially dissolved on being boiled in muriatic acid, and that consequently no quantitative method of separating it from tin can be founded upon its insolubility in hydrochloric acid.—*Journ. für Prakt. Chem.*, xxxv. p. 313.

New Method of distinguishing the most minute Arsenical Spots from those of Antimony. By M. LASSAIGNE.

This process consists in exposing the spots obtained with Marsh's apparatus to the action of the small quantity of vapour which is evolved by iodine at a temperature of 53°–59° F. The arsenical

spots assume a pale yellowish-brown colour, which becomes lemon-yellow by exposure to the air for a few minutes, and subsequently disappears by continued exposure to the air or a gentle heat. The antimonial stains, under the same circumstances, become deep reddish-yellow; this turns orange on exposure to the air, and is subsequently permanent. To observe this reaction, which is developed at ordinary temperatures in 10–15 minutes, the porcelain capsule, on which the spots obtained with Marsh's apparatus are deposited, should be inverted upon a saucer, in the centre of which a small quantity of dry crystallized iodine has been placed. We have stated that the yellow spots, produced from the arsenic by iodine, gradually disappear in moist air; when the process is completed, if a concentrated solution of sulphuretted hydrogen be poured into the capsule containing them, those parts which were covered by the primary spots become pale yellow from the conversion of the arsenious acid produced by the action of moist air upon the iodide of arsenic into the yellow sulphuret of arsenic. These spots, which are of the same size as the former, disappear instantly when treated with a dilute solution of ammonia, which dissolves them. The ioduretted antimonial spots do not disappear in the air; after having been treated with solution of sulphuretted hydrogen and assumed an orange-yellow colour, they resist the action of dilute ammonia for a considerable time, which thus constitutes a new means of distinguishing the arsenical spots. In addition to these reactions, there is another decisive character in which we place great confidence. An alcoholic solution of iodine instantly dissolves the arsenical spots, and on spontaneous evaporation leaves a lemon-yellow stain. The antimonial spots remain unaltered when touched with this solution; but on spontaneous evaporation, the black antimonial stain is replaced by an orange-red one, composed of iodide of antimony, which is permanent at a gentle heat (86° – 104° F.), and on exposure to the air for several days is slightly altered in tint only. Solution of ioduretted hydriodic acid acts like the alcoholic solution of iodine, but more energetically; we therefore prefer it to the former liquid. An ioduretted solution of iodide of potassium instantly dissolves the arsenical spots, whilst it exerts no immediate action upon the antimonial ones.—*Comptes Rendus*, Dec. 15, 1845.

PATENTS.

Patent granted to James Thompson, Cornwall Road, Lambeth, for Improvements in the Preparation and Application of various Farinaceous Products.

THIS invention consists in improvements in preparing flour and other products from potatoes, and in the machinery for manufacturing the same.

The potatoes are steeped in water for 5 or 6 hours, and then thrown into a cylinder (composed of a number of wooden bars, an inch or two apart), revolving in a trough filled with water. By the revolution of the cylinder, the potatoes are freed from dirt and from

the greater portion of their skins ; the dirty water runs off through an outlet in the bottom of the trough, while a continuous supply of clean water is kept up from a pipe overhead. After this the potatoes are reduced by rasping to a fine pulp, the fibrine contained in which is then separated from the starch by subjecting it to a number of washings in cylindrical sieves of metallic gauze : the starch passes through the sieves in solution, and the fibrine, or the greater portion thereof, remains in the sieves. Common salt is added to the starch-liquor, in the proportion of about one ounce to each gallon of the liquor, which has the effect of throwing up any small particles of fibrine that may not have been separated by the preceding operation ; and from the purified starch-liquor a fine flour is obtained by subsidence, rewashing, drying, sifting, &c., as practised by manufacturers of potato-starch. The fibrine is converted into yeast, by first subjecting it to great pressure, to expel the water ; it is then dried and ground into meal ; this meal is mixed with a decoction of hops, and the mixture is strained and left for a short time to ferment, when it becomes converted into yeast suitable for baking and other fermenting purposes.

The potato-flour is used for improving the quality of bread, by adding to the liquor used in making the dough about one or two pounds of the potato-flour for each sack of wheat-flour employed ; or the potato-flour may be made into a jelly with boiling water, and worked up with the dough. This addition causes the bread to keep sweet and moist much longer than usual, and prevents it from crumbling. Potato-flour is also mixed with the ingredients used in making pastry in about the same proportion as for bread, and it causes the article so made to be much lighter than usual. A fancy-cake may be made with potato-flour alone, and without butter, by beating up the yolk of eggs with sugar, thickening with potato-flour, flavouring with citron or lemon, and then baking it.—Sealed Dec. 20, 1844.

Patent granted to Simon Snyder, Dayton, Ohio, for Improvements in tanning Hides and Skins.

This invention consists in preparing hides and skins for being tanned, by making, either on the flesh or grain side, a great number of indentations or small holes through them, in order that the tannin may enter more freely and perfectly into the hides and skins ; the chief object of the invention being to expedite the process of tanning.

The most proper time for performing the operation of perforating or puncturing is when the hide or skin is in its most relaxed state, being the last time it is worked out of the "bate" or "grainer," and just before introducing it into the tan-liquor ; but it may be perforated at other stages of the cleansing or tanning process. The holes or indentations may be made by a hand instrument, with a surface of steel points, to be applied to the hide or skin, and caused to penetrate by pressure, or by striking with a mallet ; or the perforations may be formed by passing the hide or skin under or over a cylinder or flat surface, covered with steel points, to the number of from 100 to 300 to the square inch.—Sealed June 28, 1845.

THE CHEMICAL GAZETTE.

No. LXXXII.—March 16, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Alloxan, Alloxanic Acid, and some new Products of Decomposition of Uric Acid. By ADOLPH SCHLIEPER.

[Concluded from p. 101.]

Nitro-hydurilic Acid.—This compound is obtained as follows:—Hydurilic acid is made into a paste with water, and $\frac{1}{3}$ — $\frac{1}{2}$ its volume of nitric acid added; as soon as it is heated, a lively reaction ensues, nitrous and a little carbonic acid being evolved. The decomposition is kept up by the application of a gentle heat, until the evolution of gas entirely ceases on cooling the liquid. When perfectly cold, the mass was diluted with water, and the new product filtered and washed, as it is perfectly insoluble in cold water. Some other products appeared to exist in the filtered liquid; on evaporation, it yielded alloxan.

The new substance thus produced is readily soluble in concentrated sulphuric acid, and is precipitated from it by water in the form of a white powder; this proceeding was adopted to obtain it in a state of perfect purity. It is soluble with difficulty in hot water, insoluble in alcohol and ammonia; it is soluble in potash without any evolution of ammonia; the alkaline solution is re-precipitated by acids, and has an acid reaction. Concentrated nitric acid dissolves it, and it is again thrown down on the addition of water. When heated in the dry state, it burns like gunpowder. For analysis it was dried at 212°. It yielded—

	I.	II.		
Carbon	23.03	23.21	8 =	600.0
Nitrogen	20.38	20.54	3	531.0
Hydrogen	1.21	1.24	2	25.0
Oxygen	55.38	55.01	14	1400.0
				2556.0

In the formation of this body the following combination ensues:—

2 at. hydurilic acid	C ²⁴ N ⁶ H ⁶ O ¹⁸
3 at. nitric acid	N ³ O ¹⁵
9 at. oxygen	O ⁹

Forming 3 at. of nitro-hydurilic acid C²⁴ N⁹ H⁶ O⁴²
Chem. Gaz. 1846. G

The alloxantine, which had subsided from the solution of the abnormal alloxan in obtaining the hydurilic acid, on treatment with nitric acid left a white pulverulent substance, which was not affected by its continued action. It is insoluble in cold water, more soluble in hot, is again deposited on cooling and evaporating the solution, and is readily soluble in ammonia; the solution on drying becomes gummy, and yields a white precipitate with nitrate of silver, which blackens on boiling. This substance is soluble in solution of potash, ammonia being evolved; on evaporation, the potash salt crystallizes in minute warts; it is not precipitated by muriatic acid, but is so by acetic acid in small granular crystals; the precipitation is much hastened by the addition of alcohol. The substance is soluble in concentrated sulphuric acid, and precipitated from the solution in small quantity only on the addition of water. Concentrated nitric acid does not act upon it. From these properties this substance was regarded as an ammoniacal compound of a new acid. To obtain the latter pure, the substance was boiled with solution of potash until the smell of ammonia had entirely disappeared; it was then precipitated with acetic acid and alcohol. The precipitate still contained a considerable amount of potash. Two experiments which were made on it showed the presence of a new substance, into which the original body had been converted by the continued ebullition with potash; thus its alkaline solution was now perfectly precipitated by the addition of acid. The precipitate caused by acetic acid was again dissolved in potash, and the solution whilst hot treated with excess of muriatic acid; when the liquid cooled, the new acid separated as a delicate white crystalline powder. The pure acid is insoluble in cold water, soluble in a considerable quantity of hot water, again separating from it on cooling; soluble in potash, being precipitated by acids from the alkaline solution; insoluble in ammonia, even on ebullition; soluble in strong sulphuric acid, insoluble in nitric acid. It yielded on analysis—

Carbon	35.97	10 =	750.0	36.29
Nitrogen	16.98	2	354.0	17.13
Hydrogen	3.21	5	62.5	3.06
Oxygen	43.84	9	900.0	43.52
				2066.5

Hence its formula is $C^{10} N^2 H^4 O^8 + HO$. The relation of the volume of nitrogen to that of carbonic acid was as 1 : 5.

Products of Decomposition of Alloxantine.—If a solution of alloxantine be rapidly boiled down to a small volume with excess of muriatic acid, it undergoes partial decomposition. Another white pulverulent body separates in admixture with the alloxantine, which subsides on cooling; the former can be freed from the alloxantine by treatment with nitric acid, in which it is insoluble. This substance is a new acid, which I shall call—

Allituristic Acid.—To obtain it pure, recrystallization from water is all that is necessary. It was soluble in about 15–20 parts of boiling water, forming a yellowish fluid, which could not be decolorized by

animal charcoal. When the solution cooled, the new acid separated as a voluminous crystalline powder of a somewhat yellowish colour. It is soluble in concentrated sulphuric acid, and is precipitated unchanged on dilution with water. When heated with nitric acid, it undergoes no change. Allituristic acid dissolves in potash, ammonia being evolved, but it is completely decomposed by it; the alkaline solution of this substance gives white precipitates with acids. It was dried at 212° , and burnt with chromate of lead. It yielded—

	I.	II.			
Carbon	36.24	36.23	6 =	450.0	36.24
Nitrogen	28.19	28.18	2	354.0	28.19
Hydrogen	3.32	3.44	3	37.5	3.02
Oxygen	32.35	32.25	4	400.0	32.65

Its formula is $C^6 N^2 H^2 O^3 + HO$.

The allituristic acid was boiled with solution of potash as long as ammonia was evolved, and whilst boiling hot was precipitated by muriatic acid. The yellowish-white precipitate thus produced was subjected to analysis after being well-washed. It was dried at 212° , and burnt with chromate of lead; the potash was estimated as sulphate. It yielded—

	I.	II.	III.	IV.		
Potash	12.63	12.64	..	..	1 =	589.9 12.48
Carbon	..	..	28.52	28.76	18	1350.0 28.57
Nitrogen ..	..	..	18.69	18.85	5	885.0 18.73
Hydrogen ..	..	..	2.27	2.23	8	100.0 2.11
Oxygen	..	..	..	..	18	1800.0 38.11
						4724.9

The solution of alloxantine, which was filtered from the allituristic acid in the preparation of the latter, and which from its reactions contained merely nitric acid, alloxan and parabanic acid, was treated with sulphuretted hydrogen to remove the alloxan; after separating the alloxantine by filtration, the solution was heated and evaporated to obtain the parabanic acid it contained, a little nitric acid being previously added to convert the dialuric acid produced by the sulphuretted hydrogen also into parabanic acid. The liquid soon became turbid. After it had been evaporated to one-third of its volume, the yellowish precipitate which was produced was separated by filtration; it was subsequently ascertained to be the ammonia salt of a new acid, diluturistic acid. The remaining liquid contained scarcely anything but parabanic acid, which was obtained pure by recrystallization.

Diluturistic Acid.—The new substance merely requires to be dissolved in hot water in order to purify it; on cooling, splendid, shining, yellow laminæ separate. The acid itself could not be separated, being retained in its compounds with remarkable force. The ammonia salt is almost insoluble in cold water, more soluble in hot; the solution cannot be decolorized by animal charcoal; the yellow colour appears to be peculiar to the compounds of this acid. It is perfectly insoluble in ammonia, and its crystals do not lose any of

their lustre in it. It is soluble in dilute solution of potash, ammonia being evolved; it is not dissolved by it when concentrated, because the potash compound which is formed is insoluble in it. Acids cause a yellowish-white precipitate in the alkaline solution. It is moreover perfectly insoluble and undecomposed by strong nitric acid. It dissolves with ease in strong sulphuric acid, and is completely precipitated from it by water. When the dry salt is heated, it burns readily, and glimmers like tinder. It was dried at 212° , and burnt with chromate of lead. It yielded—

	I.	II.			
Carbon	25.76	25.37	8 =	600.0	25.18
Nitrogen.....	30.39	29.93	4	708.0	29.71
Hydrogen	3.29	3.31	6	75.0	3.15
Oxygen	40.56	41.49	10	1000.0	41.96
				2383.0	

If we regard the ammonia salt as a compound of 1 atom of the acid in question with 1 atom of ammonia, we obtain the following formula for the ammonia salt:— $C^8 N^3 H^2 O^9 + NH^4 O$, and for an atom of the supposed anhydrous acid $C^8 N^3 H^2 O^9$. We must however arrange this acid in the class of bibasic acids; its formula will then be $C^8 N^3 HO^8 + 2aq$, and that of the ammoniacal salt analysed $C^8 N^3 HO^8, NH^4 O + HO$.

The neutral potash salt of this acid is obtained by boiling the ammonia salt with dilute solution of potash until the whole of the ammonia is evolved; if alcohol be then added to the hot solution, until the troubling which is caused ceases to be completely redissolved, a copious crystallization ensues, on cooling and repose. Small shining, and large needles of a beautiful lemon-yellow colour are formed; they are insoluble in alcohol, and soluble with tolerable ease in cold water. When heated to a certain point, the salt explodes, becoming completely decomposed, without the slightest separation of carbon, into cyanate of potash, carbonic and cyanic acids, both of which latter escape in the gaseous form. When dried at 212° , the salt had not lost its lustre nor any water. Its formula is $C^8 N^3 H O^8, 2KO + 3HO$.

The solution of this salt is precipitated on the addition of acids; an acid potash salt separates as a yellowish-white powder. The potash cannot be removed from it any more than the ammonia from the ammonia salt; it is difficultly soluble in cold water, more readily soluble in hot; when the aqueous solution cools, it is deposited in the crystalline form. It is not decomposed by concentrated sulphuric acid; it dissolves in it, and is precipitated from it by water, the amount of potash remaining unchanged. When heated, it behaves like the neutral salt. It was dried at 212° and analysed. Its formula is $C^8 N^3 HO^8, KO + 2HO$. The solution of this salt, like that of the acid ammonia salt, is not precipitated by nitrate of silver. In obtaining the silver salt, the solution of the neutral potash salt was mixed with solution of nitrate of silver. It then immediately separated as a bright lemon-yellow precipitate. Its formula is $C^8 N^3 HO^8 + 2AgO$.

This acid may be regarded as a conjugate acid, in which 3 atoms of cyanic acid are combined with 2 atoms of carbonic acid and water. This view is supported by its reactions, its extremely easy decomposition into these two acids by heat, the detonation of its salts, and its resistance to the action of mineral acids.—Liebig's *Annalen*, Oct. 1845.

On some Double Salts of the Magnesian Group.

By J. ISIDORE PIERRE.

The author, who has examined with great care the salts of this group, including those of magnesia, oxide of copper, zinc, nickel, cobalt, manganese and iron, observes, that it is well known that Prof. Graham has stated, with respect to the sulphates of the above-named bases, that one of the equivalents of water cannot be eliminated, except at a much higher temperature than is required for the others; that this equivalent may be replaced by an equivalent of a salt, so that the double salt formed contains one equivalent less of water than if each of the two simple sulphates had brought all its water of crystallization into the molecule of the double salt resulting from their combination.

M. Pierre states that the results which he has obtained do not confirm those of Prof. Graham; he found that sulphate of zinc contains, as generally admitted, 43.72 per cent., or seven equivalents of water; and he ascertained that by exposing it for a long time to a temperature of 230° Fahr. and a current of dry air, it lost 43.6 per cent., or the whole of its water, which is at variance with Graham's result, who found that it required a heat of 400° Fahr. to expel the seventh equivalent of water.

Double Sulphate of Zinc and Potash.—This salt is readily prepared by mixing together hot solutions of equivalents of sulphate of zinc and bisulphate of potash, and allowing crystallization to take place. The crystals are beautiful small, milk-white parallelogrammic tables; this salt is soluble in two and a half times its weight of boiling water, but much less soluble in cold water, for it crystallizes abundantly on the cooling even of an unsaturated solution.

When exposed gradually to a heat of 356° to 392° Fahr., it effloresces without fusing in its water of crystallization, which it loses completely and pretty rapidly at this temperature, the amount being 27.49 per cent. The author's analysis gives as the formula of this salt, $\text{ZnO}, \text{SO}_3; \text{K}_2\text{O}, \text{SO}_3 + 7\text{HO}$, which indicates, as he shows, 27.32 per cent. of water instead of 24.49, the experimental result.

In this case it is therefore to be remarked, that the sulphate of zinc retains the seven equivalents of water which it possessed in its simple state.

Double Sulphate of Zinc and Magnesia.—M. Pierre observes, that it is generally supposed that these two sulphates may combine in all proportions; having found that sulphate of zinc in the double salt which it forms retains its seven equivalents of water, the author ob-

serves that if sulphate of magnesia did the same, the double salt should contain fourteen equivalents of water.

This salt is readily obtained by mixing its equivalents and crystallizing; it forms very fine oblique rhombic prisms, which are by pressure separated into very fine needles; when quickly heated to 212° to 248° Fahr., it loses part of its water; at 392° Fahr. it retains two equivalents of water, and these cannot be expelled at a temperature lower than 482° to 500° Fahr.

When heated slowly and progressively, this salt effloresces without fusing in its water of crystallization; it may in this mode be deprived of the whole of its water of crystallization without being fused; it merely agglutinates slightly.

The formula of this salt derived from analysis is $\text{ZnO}, \text{SO}^3, \text{MgO}, \text{SO}^3 + 14\text{HO}$, which indicates 47.17 per cent. water; the loss of water by experiment was 47.12; the salt heated to 392° Fahr. retained ten equivalents of water.

From the preceding and the analyses of various other salts which the author prepared, he arrives at the following among other conclusions:—

1. Sulphate of zinc, containing seven equivalents of water, retains the whole of it in the compound which it forms with the alkaline or alkalino-earthly sulphates.

2. The sulphates of zinc and magnesia combine equivalent to equivalent, and the resulting compound contains a quantity of water equal to the sum of the quantities which both salts contained when separate, that is to say, fourteen equivalents, if the double salt crystallizes at common temperatures.

3. The simple sulphates of zinc, copper and nickel yield all their water at a little above 212° in a long-continued current of air, instead of retaining one equivalent, at 400° Fahr., as stated by Prof. Graham.

4. The simple sulphates of zinc, magnesia, copper and nickel combine with other sulphates, or with each other without elimination of the water.—*Ann. de Ch. et de Phys.*, Fevrier 1846.

Presence of Arsenic in Soot.

MM. Mareska and Lados have discovered arsenic in soot. They estimate the quantity at the $\frac{1}{2400}$ th of a grain in a pound. It is most probably derived from the iron pyrites of the coal.

In the case of a female who was poisoned with arsenic in the fourth month of pregnancy, they found traces of arsenic in the fœtus, uterus and placenta, the latter containing a larger proportion than the fœtus. No appreciable trace could however be detected in the *Liquor amnii*.—*Gaz. de Hôpitaux*, Jan. 1846.

ANALYTICAL CHEMISTRY.

On a new Method of estimating Copper. By J. PELOUZE.

HITHERTO gold and silver were the only metals which could be determined by quick and at the same time accurate processes. The various methods applied to the estimation of the other metals are certainly good in the majority of cases; but they are subject to several inconveniences, the principal of which is the length of the operations and the delicacy of the methods. From this state of things, the history of the most important alloys are but imperfectly known. In commerce and the arts the question of time frequently prevails over all others, and an analysis which would be extremely useful if it could be done quickly, loses its interest if the result has to be delayed. Now this does not apply merely to the commerce in metals and metallurgical operations, but to all establishments in which castings are made.

The preceding observations suffice to show the utility of a process combining great precision with quick execution. In my situation as assayer of the Mint, I am able to appreciate every day the extreme importance, the accuracy and rapidity of the mode of analysis of alloys of silver, the discovery of which is due to M. Gay-Lussac; knowing moreover all the advantages which the arts have derived from the standard solutions so frequently introduced by that illustrious chemist, I endeavoured to estimate the copper by processes more or less similar, being persuaded that after gold and silver there is no metal the determination of which is of greater importance, as it enters into all the alloys most commonly employed.

I have arrived at this result by several different ways, based principally on the phenomena of precipitation and simultaneous decoloration. The ingenuity with which M. Barreswill* turned to account the solution of copper in tartaric acid and potash to solve a very important and difficult question, the estimation of sugar, has been highly appreciated by chemists. I hoped that by modifying the cane-sugar by acids, I should be able to form standard solutions, and to ascertain with them the proportions of copper contained in an alloy by treating this successively with nitric acid, tartaric acid and potash; but after numerous experiments I had to abandon this process; the approximations, sometimes very satisfactory, varied however frequently three, four and five-hundredths from the real proportions of copper without my being able to ascertain the cause. On substituting for the sugar modified by acids a solution containing a known quantity of protochloride of tin, I obtained results much more accurate.

The following is a description of this second method:—I dissolve a known weight of copper, for instance 1 grm. in nitric acid, add successively to the liquid, solutions of tartaric acid and caustic potash, and obtain thus a solution of an intense blue colour, into which I

* Chem. Gaz., vol. ii. p. 544.

pour while it is boiling a dilute solution of protochloride of tin. The protoxide of tin eliminated by the alkali absorbs half the oxygen of the oxide of copper and precipitates that metal in the state of insoluble protoxide. The decoloration of the liquid indicates the end of the experiment.

Tin, zinc, lead, arsenic and antimony, all of which may occur in copper alloys, do not interfere with the preceding reaction; they form oxides or acids, which remain dissolved in the potash, so that if it had required 30 cubic centimetres of the standard solution of tin to precipitate 1 grm. of pure copper, a similar number of divisions of the test-tube would represent the same weight of copper in those different alloys*.

The other process, that which I have finally adopted, is based on the same principle, but the copper is dissolved in ammonia, which heightens the colour far more considerably than the tartaric acid and potash. For the protochloride of tin I substitute an alkaline monosulphuret, and especially that of sodium (colourless crystallized hydrosulphate of soda), which is an article of commerce.

The following is the mode of proceeding:—1 grm. of very pure copper is dissolved in 7 to 8 cubic centimetres of commercial nitric acid, the solution is diluted with a little water and an excess of ammonia added to it (20 to 25 cubic centimetres); we thus obtain a very deep blue solution. On the other hand, some sulphuret of sodium is dissolved in water (the quantities in this solution may vary without any inconvenience; we may take, for instance, 110 grms. to 1 litre of distilled water) and poured into a tube graduated and divided into tenths of cubic centimetres; the ammoniacal liquid is heated to boiling, and the solution of the sulphuret gradually added to it. If we suppose that it required 31 cubic centimetres to decolorize 1 grm. of copper, we have a standard solution of known strength.

Upon this a known weight, for instance 1.100 grm. of the alloy to be analysed, is dissolved in nitric or nitro-muriatic acid, the solution supersaturated with ammonia, heated to boiling, and some of the standard solution of sulphuret of sodium added to it until decolorized, taking care to add from time to time a little dilute ammonia to replace that which is evaporated. The decrease in the depth of the blue tint points out that the end of the experiment is more or less near, and that it is requisite to add the last portions of sulphuret in drops. When the operation is supposed to be finished, the number of the divisions employed for the decoloration is read off; if 31 were required, then there is 1 grm. of copper in 1.100 of the alloy; if 24.8 were employed, by dividing this number by 31 and the quotient by 1.100, we find $\frac{7.27}{1000}$ †.

This mode of operating suffices in most cases; it is not liable to

* I propose to return to this process, and to see whether it is applicable to the case where the copper is alloyed with cobalt or nickel.

† The ammoniacal liquor from which the copper has been precipitated does not remain long colourless; it gradually becomes blue, because the sulphuret of copper absorbs oxygen, and is converted into sulphate.

an error of more than five to six-thousandths; but still greater accuracy is obtained by completing the decoloration of the blue liquid with a very weak solution of sulphuret, with a liquor containing for instance in every cubic centimetre the quantity of sulphuret required to precipitate 2 milligrms. of copper. In this respect I have followed the instructions recommended by M. Gay-Lussac for the analysis of alloys of silver in the moist way.

It was necessary to ascertain that the presence of those metals which are usually alloyed with copper do not give rise to any error in the estimation of the latter. On this subject I made numerous experiments, which led to the most satisfactory results. I added to known weights of very pure copper, variable proportions of tin, zinc, cadmium, lead, antimony, iron, arsenic and bismuth, and I constantly found the same weight of copper to within two to three-thousandths. I have requested a great number of chemists to repeat these experiments on variable quantities of copper mixed with the above metals, and whose weights were unknown to them; and they have always correctly determined the proportions of copper to within some thousandths.

Another proof that the metals above mentioned are not affected by the sulphuret of sodium while a trace of copper remains to be precipitated is the following:—When the sulphurets of zinc, cadmium, tin, lead, bismuth and antimony are placed in contact with an ammoniacal solution of nitrate of copper, they decolorize it, some in the cold, others with the assistance of heat; which proves very evidently that these sulphurets cannot exist, except perhaps for an instant, in a solution of copper. Their formation subsequently to the decoloration has no influence on the result of the analysis, as the termination of this is judged of by the decoloration of the liquid, without paying the least attention to the precipitates which subsequently form; or if any attention is paid, it is only with a view to obtain some knowledge of the nature of the metals which accompany the copper. Thus if the alloy consists of copper, lead, tin and zinc, the presence of the zinc is readily detected by the white precipitate which succeeds the black precipitate of sulphuret of copper, the lead and tin being precipitated at the outset by the ammonia. I hope indeed to succeed in estimating the zinc itself by the volume of the solution of sulphuret requisite to precipitate that metal starting from the moment of the decoloration of the copper. Cadmium, like zinc, is precipitated immediately after the copper. The very moment the liquid is observed to be decolorized, a beautiful pure yellow precipitate of sulphuret of cadmium is formed if the addition of sulphuret be continued.

I have mentioned a considerable number of metals whose presence does not prevent the success of the new process, and fortunately they are such as are most frequently met with in the impure coppers of commerce or in the ores or alloys of copper. It is evident that cobalt and nickel, yielding oxides soluble in ammonia, which they colour, would prevent the application of the new process; silver offers no obstacle, only after the alloy has been dissolved in nitric acid, the

silver must be precipitated by an excess of hydrochloric acid and the chloride washed on a filter. The liquid and the wash-waters are employed for the determination of the copper. On estimating the silver by the moist way and the copper by the new process, the proportions of the two metals are readily determined to within two to three-thousandths. Tin, which frequently occurs in the alloys of copper, exists in the ammoniacal nitrate of copper in the state of stannic acid. This acid remains for a long time in suspension, and it sometimes happens that it retains a slight portion of sulphuret of copper, which colours it. In every case it prevents the transparency of the liquid, and it is difficult to judge of the end of the decoloration. I have found a sure method of obviating this inconvenience: I had observed, when operating on the alloys of copper, tin and lead, that this last metal, when precipitated in the state of oxide by ammonia, carries with it some stannic acid, with which undoubtedly it combines, and that the liquids then become clear with great rapidity. I took advantage of this observation, without which the two or three last hundredths of copper would have been difficult to estimate, and I added to all the assays of alloys of copper and tin or antimony, a solution of nitrate of lead prepared beforehand; to render the liquids clear, it suffices to add 1 cubic centimetre of a solution containing 1 decigram. of lead.

Another observation which I made rectifies an error propagated in all manuals of chemistry. The precipitate, prepared by pouring a soluble sulphuret into a hot solution of a copper salt, was considered to be a bisulphuret; but it is a combination of sulphuret and oxide of copper, an oxysulphuret consisting of 5 equiv. of sulphuret and 1 equiv. of oxide. I was led to examine it from remarking that it required far more sulphuret of sodium at the ordinary temperature than at the boiling-point of the liquids, to precipitate the same weight of ammoniacal nitrate of copper, and that a solution of copper is decolorized on boiling it with the precipitate of bisulphuret, which is explained by the combination of the sulphuret with the oxide of copper.

Independently of the analysis which I have made of this new compound, I have observed that bisulphuret of copper, when well-washed and boiled with sulphate of copper, removes the oxide from this salt, and leaves nothing in the water but pure sulphuric acid.

Another important property of the ammonia, besides that of heightening the colour, is that it prevents the salts of copper being precipitated by the hyposulphites, and without which it might perhaps have been impossible to estimate the copper by means of solutions of the alkaline sulphurets. It is known that they occur almost always in the alkaline sulphurets, and that they are moreover produced from them by contact with the air, and that they decompose the neutral and acid salts of copper, giving rise to a precipitate of sulphuret of copper; but the ammonia prevents this decomposition, not merely as regards the hyposulphites, but likewise with respect to the sulphites and sulphohyposulphates. Moreover, when it is present in suitable proportion, it equally prevents the precipitation of the

same salts by the carbonates and alkaline oxides. This is the more important, as all these bodies occur or may occur in the soluble sulphurets.

A solution of sulphuret of sodium becomes weaker by contact with the air; but this alteration is very slow, and it is even unnecessary to change the liquid as long as any remains in the flask, in which a quantity had been prepared. The only precaution to be taken, and it is one which applies to all the standard solutions, is to determine, previous to each assay, the actual strength of the sulphuret with a known weight of pure copper. I can already state that this method, applied to the analysis of copper ores, yields results of the greatest accuracy, and I have no doubt it will render great services in the administration of the Mint, the government foundries, and other metallurgical works.

In conclusion, I may add, that two young chemists, working in my laboratory, have attempted to estimate iron and lead by means of standard solutions; their investigations are sufficiently advanced to lead me to expect a satisfactory result.—*Comptes Rendus*, Feb. 2, 1846.

On the Quantitative Determination of Mercury. By E. MILLON.

MM. Ettling and Bunsen have had recourse to a particular method for the determination of mercury, based upon the reduction of the mercury by the dry way. MM. Erdmann and Marchand made this method the base of the means they adopted to determine the new equivalent of mercury*.

I have endeavoured to render it as easy and expeditious as possible without depriving it of any of its exactitude. The most important modification consists in the employment of a current of hydrogen gas to assist in the reduction of the mercurial compound. Hydrogen may be more easily obtained in a regular current than most other gases; it greatly facilitates the decomposition of all mercurial compounds, and its continued current provokes the expulsion of the water which accompanies the reduction of mercurial compounds, at the same time that it favours the condensation of the mercury in the expansion of the tube in which it is to be collected and weighed.

The dry gas is passed through a tube containing copper turnings heated to redness. This was found to be the most efficacious method for preserving the perfect metallic lustre of the mercury obtained in the analysis. It is in all cases a convenient means of purifying hydrogen.

On leaving the tube with the copper turnings, the gas enters the tube containing the mercurial salt. This tube should be from 14 to 16 inches long, and of the diameter of an ordinary tube for organic analysis. At a small distance from its free extremity, the tube should be contracted, and then again contracted and drawn

* Chem. Gaz., vol. ii. p. 400.

out at the point and curved upwards; it will then present a space of from 3 to 4 inches comprised between the two contractions.

A little asbestos is first placed in the tube next the first contracted part; then caustic lime, in small fragments, to the extent of 6 to 8 inches; the mercurial compound is then introduced, the quantity of which may vary from 1 to 4 grms. (15·5 to 62 grms.), and then the tube is filled with caustic lime similar to the other. In the analysis of the nitrate of mercury, the lime should be replaced by metallic copper. The tube is now placed in the furnace used for organic analysis; it receives the current of hydrogen gas at its wider and uncontracted extremity, and heat is applied exactly as in an organic analysis. The ignited charcoal is gradually approached to the part of the tube containing the mercurial compound, and then a few pieces are placed behind it to prevent the condensation of the metal there.

The water is first seen in the portion of the tube between the contractions; it is dissipated by gently heating it; this part of the tube is then allowed to cool, and the mercury now soon makes its appearance, condensing in its turn without any difficulty; at the end of the operation this part of the tube containing the mercury is separated by slightly moistening the heated tube; the portion of the tube is weighed with the mercury it contains, the mercury poured out, the particles adhering to it removed by nitric acid; it is then washed, dried and weighed again. The difference of the two weights gives the weight of the mercury.

The author assures us he has been able to propel 3 and 4 grms. of mercury from one extremity of the tube to the other, condensing it between the contracted parts without the smallest loss. The following are the results obtained from pure bichloride of mercury:—

First Analysis.

Salt employed.	Mercury obtained.	Per cent.
2·217	1·899	73·87

Second Analysis.

2·5785	1·9035	73·82
--------	--------	-------

In calculating the atomic weight of mercury from that of chlorine, expressed by 442·64, we obtain for the equivalent of mercury—

First experiment	1251·02
Second experiment	1248·24

These numbers agree very closely with those obtained by Erdmann and Marchand, who give 1250·9 as the atomic weight of mercury, a number differing greatly from that of 1265·92, hitherto adopted. —*Ann. de Chim.*, 1846.

CHEMICAL PREPARATIONS.

On a new and simple Method of preparing Chloric Acid.

By Prof. BÖTTGER.

EVERY chemist is aware of the difficulties connected with the preparation of even minute quantities of chloric acid by means of hydrofluosilicic acid. I have therefore endeavoured to discover a more simple and quicker process, which on the whole is, it is true, somewhat more expensive, but in every other respect is certainly preferable to all the methods hitherto known. The question turned on the employment of some other commercial acid instead of the hydrofluosilicic acid, which would yield, when combined with soda, a salt insoluble or sparingly soluble in water. It certainly appears most advisable, in decomposing a chlorate for the purpose of obtaining the acid, to use in future the readily soluble soda salt instead of the sparingly soluble potash salt. From experience, I was led to believe that oxalic acid would be best adapted, the binoxalate of soda being a very sparingly soluble salt. The following is the process:—A solution of chlorate of soda is first prepared by decomposing bitartrate of soda with chlorate of potash in the following manner:—7 parts by weight of crystallized carbonate of soda and $7\frac{1}{2}$ parts by weight of tartaric acid are dissolved in 24 parts boiling water, and to this boiling solution is added one of 6 parts by weight chlorate of potash in 16 parts water, likewise heated to 212° F., at the same time agitating the mixture. As soon as this is done it is taken from the fire and allowed to cool, in order that the bitartrate of potash formed may separate properly; upon which it is poured on a double paper filter, and to the filtered liquid is added a saturated solution of oxalic acid, consisting of 6 parts by weight oxalic acid, and 18 parts of water heated to not above 134° ; the whole is then well-agitated, and the vessel placed in an ordinary refrigerating mixture, formed of commercial muriatic acid and sulphate of magnesia, for the better separation of the oxalate of soda, which is then entirely and easily removed by a simple filtration. The chloric acid thus obtained is, it is true, not absolutely pure, but still sufficiently so for most chemical and technical purposes; for instance, for the preparation of the chlorate of barytes, which is so much consumed in the manufacture of fireworks. To obtain a chemically pure and at the same time more concentrated acid, the solution above obtained should be treated with recently precipitated carbonate of barytes, avoiding any rise of temperature; but the solution of the barytic salt may now be evaporated over the fire, and the large beautiful crystals which soon form, are pulverized, dissolved in a little water, and decomposed with a corresponding quantity of sulphuric acid.—*Liebig's Annalen*, Jan. 1846.

On a new Method of preparing Lactate of Iron. By M. LEPAGE.

The author proposes the following plan for the preparation of this salt, which yields satisfactory results, and is much more expeditious than the old process:—

Lactate of lime	100 parts.
Boiling water	500 ...

Dissolve and filter.

Next dissolve 68 parts of pure crystallized sulphate of iron in 500 parts of distilled water, and filter. Mix the two solutions in a flask, and slightly acidulate the liquid with lactic acid. The decomposition may be aided by a gentle heat, and when this is accomplished, the liquid may be filtered to separate the sulphate of lime, and afterwards rapidly evaporated in an iron or porcelain vessel. If the latter be used, some iron filings must be added. When its bulk is reduced one-half, it may be again filtered and allowed to crystallize. The mother-liquor, decanted and carefully evaporated, will yield a fresh crop of crystals. These may be collected on a funnel, washed with a little alcohol, and dried on blotting-paper. The salt thus obtained is quite white, and its solution in distilled water is not affected either by nitrate of barytes or oxalate of ammonia.—*Med. Gaz.*

On the Preparation of the Lactate of the Protoxide of Iron.

By M. CASSEBAUM.

The author recommends Wöhler's method* for this purpose, taking care however to prevent the temperature from rising above 113° to 122°, so as not to prevent the formation of the lactic acid. He prepared the protolactate of iron in the same way by pouring 12 oz. of water over 1 oz. of milk-sugar and the same quantity of iron-filings, and digesting the liquid heated to 86° with a piece of the inner membrane of a pig's gut of about the size of the hand. In testing the preparation as to its purity by ignition, care must be taken not to expose it to too high a temperature before weighing, as it readily parts with its 3 equiv. water of crystallization.—*Archiv der Pharm.*, xliv. p. 263.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

New Apparatus for extracting the Colouring Matter from Dye-Woods. Communicated to the Society of Industry by M. IVAN SCHLUMBERGER.

AT a meeting of your committee of chemistry, I communicated the advantages which I had found in the apparatus of M. Meissonnier for extracting the colouring matter of logwood. Some members appearing to doubt the real merit of this apparatus, or not having produced results analogous to mine on trying it, I made some fresh experiments, which I explained to your committee of chemistry, accompanied by calculations which any other person might make.

* Described at page 713 of our first volume.

In order to make decoctions of logwood, the usual method is to put a quantity of shavings of that wood into a boiler in immediate contact with the fire, together with a quantity of water sufficient to cover the wood completely, so that after boiling for some hours the wood may be quite covered. The operation is renewed twice with the same liquor, and after three successive boilings the decoctions are mixed together and evaporated to the degree required.

This operation is attended with several disadvantages. Shavings only can be employed, for if the logwood is reduced to powder it absorbs so much water that a great quantity of liquid is lost, and the shavings being rather thick the water cannot readily penetrate, for which reason the time of boiling is very much prolonged.

Notwithstanding these three long boilings, if the same wood be boiled a fourth time, a liquid pretty well coloured is obtained, which clearly shows that all the colouring matter has not been extracted.

Besides this, when decoctions of logwood are required in large quantities, very large vessels and extensive premises are necessary, as well as several furnaces, in order to produce a sufficient quantity; for the wood, when in shavings, is very bulky without being heavy, and large boilers are required for making a decoction from 50 lbs. of shavings with the necessary quantity of water. Several boilers must therefore be employed, otherwise the fire must be kept up day and night.

I will here describe, for the benefit of those persons who have not many furnaces, but who have a steam-pipe at command, a method which I have employed for some time to make decoctions in great quantities, and which I think I can recommend in this instance.

A large high narrow vat, capable of containing from about 100 to 150 lbs. of wood shavings, is mounted upon a stand or framing, and furnished with a cock below, in order to draw off the liquor. At a short distance above the cock, inside the vat, a false bottom or diaphragm, pierced with holes very close to each other, is fixed, in order to leave a space at the bottom to prevent the wood from clogging up the cock and stopping the flow of the liquor. A steam-pipe, about one-third of an inch in diameter, is carried to the bottom of the vat, which is filled with shavings. It is covered with a cloth and a cover, which is weighted, in order to prevent the steam from issuing out in too great abundance. The shavings must not be heaped up more than in the common boilers. In this state steam is allowed to flow in for an hour at least, until it escapes out in moderate quantities at the top. During this time the wood swells and becomes penetrated by the steam; then when the vat is filled with water, it will be sufficient to heat to the boiling-point, in order to obtain the first time a strong decoction. The vat is afterwards filled twice in succession, and made to boil as usual; and in the same space of time, with less labour, a much larger quantity of decoction is obtained and much more colouring matter extracted.

By the two methods just mentioned considerable time is required for each operation, and the wood is not entirely exhausted of colouring

matter; but with M. Meissonnier's apparatus much more advantageous results are attained.

This improved apparatus consists of a copper boiler of about $1\frac{1}{2}$ foot in width and about 2 feet in depth. At a short distance from the bottom of the boiler is a false bottom, pierced with a multitude of holes, which sustains the wood in the water and leaves an empty space for the boiling liquor. Into the boiler powdered wood is thrown, and it is covered first with strong wire-work, and then with a copper-plate, pierced with small holes, which cover is held firmly down upon the edges of the boiler by any suitable means. At the side of the boiler is a small lift and force-pump, of simple construction, which draws the boiling water from any suitable vessel, and forces it through a pipe into the empty space at the bottom of the boiler. The water, after passing through the wood and the pierced cover of the boiler, is run off into any suitable receiver.

In our manufactory, at the side of the pump is a boiler, heated with a coal-fire, capable of containing 450 quarts of water, which is to be boiled for each operation. After filling it and lighting the fire, the other boiler is filled with powdered logwood, spread as evenly as possible, until it contains from 84 to 90 lbs. of wood. The water having arrived at the boiling-point is then forced into the space at the bottom of the vessel containing the dyewood, and driven up through the wood. In this manner, in 2 hours, the 450 quarts pass through and extract all the colouring matter from the dyewood.

The liquor which has passed through the wood is divided into three distinct portions, in this manner:—A first portion of the decoction may be $3\frac{1}{2}^{\circ}$ Beaumé; a second, $1\frac{1}{2}^{\circ}$; a third, $\frac{1}{2}^{\circ}$; and lastly, a fourth portion of liquid very slightly coloured, which may be mixed with the water for the next operation. In this manner the most advantageous results are secured, as three decoctions, of different degrees of strength, are obtained at one working without evaporation.

When a second operation is not commenced immediately, the waste heat of the furnace is employed to concentrate the liquor.

I will compare the advantages of this apparatus with that which were previously in use.

Thus, in a boiler heated by fire, 140 lbs. of shavings and 80 quarts of water were put, and the liquor was boiled for 4 hours; this was renewed three times. For 40 lbs. of logwood it was therefore necessary to boil 240 quarts of water for 12 hours. I double these quantities, the better to compare them with those produced by the new apparatus. Thus, by the old method, for 80 lbs. of wood it was necessary to boil 480 quarts of water during 24 hours.

By the new method, when from 84 to 90 lbs. of wood are operated upon, 2 hours are necessary for heating the 450 quarts of water, and 2 hours for pumping it through the wood. Therefore, for 84 lbs. of wood it will be necessary to heat 450 quarts of water for 4 hours, effecting an economy of fuel for 20 hours' consumption. Besides this, the colouring matter is better extracted, and a great

oeconomy of labour is effected, as one man can effect two operations per diem.

Several precautions are necessary, in fact indispensable, to ensure complete success; for instance, the wood must be very evenly spread, in order that the resistance offered to the water may be equal throughout; and for this purpose the wood must be put into the vessel in small quantities at a time. A very important point is, to have the wood ground or rasped of a uniform size, without fine dust, as the particles of this latter are apt to adhere together, and offer great resistance to the water at certain parts; thus preventing the colouring matter from being extracted. I have found that the wood spreads much better by previously wetting it.

For some other woods, such as Lima and Pernambouc woods, and other red dyewoods, 600 quarts of water, instead of 450, must be employed, as the colouring matter is not so easily extracted. Quercitron cannot be operated upon, as it is too fine a powder. Cochineal does not succeed, as it swells so much on coming in contact with boiling water, that in an experiment I made I thought it would have burst the boiler.

This apparatus is, however, very advantageous for the woods above-mentioned, if the directions given are carefully followed.—*Bulletin de la Société Industrielle de Mulhouse*, as inserted in Newton's *London Journal and Repertory of Arts, &c.*

Employment of Rochelle Salt in Dyeing. By J. A. BENCKISER.

The potassio-tartrate of soda may be substituted in all cases in the dyeing of wool, both for the crude as well as for the purified tartar; it has even several advantages over it. It is pure, always of the same composition, and readily soluble in water, while the bitartrate of potash is so frequently mixed with foreign ingredients that often only 50, rarely more than 70 per cent. of pure bitartrate can be obtained from it. The impurity in the colour of the tartar may very readily injure that of the cloths; the fibrous parts of the tartar adhere to the wool, and the fragments of sulphur which frequently occur in it make spots; moreover, a portion frequently remains undissolved in the water, and is lost. The potassio-tartrate of soda is capable of decomposing a larger quantity of alum, sulphate of iron, tin-salt, &c., the whole of the tartaric acid combining with the alumina or the metal by double decomposition. Instead of 100 lbs. *Cryst. tartari* (price 70s.), there is required only 66 lbs. of Rochelle salt (price 52s.).—*Archiv der Pharm.*, xliii. p. 144.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Jan. 5, 1846. (The President, Professor Graham, in the Chair.)

"On the unequal Decomposition of Electrolytes, and the Theory of Electrolysis," by Mr. James Napier.

The author, after alluding to his former paper on this subject*, read before the Society in January 1845, and published in their 'Proceedings,' vol ii. p. 255, and reviewing the deductions then arrived at, stated that he had observed, while experimenting on electrical endosmose, that there seemed some relation between the subject now under consideration and the cause of measurable endosmose, which rendered it probable that the element of an electrolyte liberated at the negative pole, as in the deposit of a metal, might not be, as he had formerly advanced, an accurate measure of the electricity passing through the solution; but that a feeble current may be also passing, capable of causing the solid electrode to combine with the elements of the electrolyte, but not sufficient to decompose all the compound fluid through which it passes. The author then described the various experiments made to test these suggestions, the results of which were confirmatory of his supposition. Mr. Napier concluded his paper by a few remarks on the philosophy of electrolytic action. He considers that no basic element of an electrolyte is transfused by electrolytic action; but that the base of an electrolyte, which is being decomposed, is the medium or conductor of the electricity through the solution from electrode to electrode.

Feb. 16, 1846. (Prof. Brande, Vice-President, in the Chair.)

"On Atomic Volume and Specific Gravity of Elementary Bodies, their Oxides and Sulphurets," by L. Playfair and J. P. Joule.

The authors commenced by referring to their previous paper on this subject†. They had there stated that 9·8, or the volume of ice, formed a submultiple for a large class of salts. But the number 9·8 itself was made up of numbers due to the volumes of the constituents

of which it was composed, $\frac{9.8}{8} = 1.225$, which number the authors

stated was the primitive volume. In support of this view, they calculated the volumes of all the metals where the specific gravity has been taken with tolerable accuracy, and found the results to deviate from the theoretical expression by being about $\frac{1}{20}$ too small. They ascribed this deviation to the force of cohesion in the metals; and to ascertain whether this was the case, they took the specific gravity of some of the metals in a state of fusion, and found their specific gravity in this condition to give results in exact accordance with theory.

They then examined the oxides and sulphurets, and found that they gave very exact results, the force of cohesion not being so powerful; but in some of them, those commonly called the magnesian oxides, they found $5\frac{1}{2}$ unit volumes instead of 5 volumes. They therefore contended that the magnesian metals ought to have their equivalents doubled, and that their oxides, instead of being

should stand $R^2O, RO, R^2O^3, RO^2,$
 $RO, RO^3, RO^3, RO^4,$

the oxygen increasing in arithmetical progression.

* See Chem. Gaz., vol. iii. p. 112.

† *Ibid.*, vol. iii. p. 377.

The authors then examined the volumes of dimorphous and polymorphous substances, and found that the differences of volume were either expressed by the unit volume 1.225, or by a multiple of the unit volume.

“On the Employment of Phosphoric Acid for detecting Alumina,” by Mr. J. C. Nesbit.

This process depends on the insolubility of the phosphate of alumina in acetic acid. If alumina is to be separated from the ashes of plants, the oxide of iron, if present, is to be precipitated with the alumina as phosphate by the addition of phosphate of soda, acetate of ammonia and acetic acid. This precipitate is then to be boiled with pure caustic potash, which will dissolve the phosphate of alumina; this latter may then be reprecipitated by muriate or acetate of ammonia and acetic acid.

PATENTS.

Patent granted to John Greenwood, John Mercer and John Barnes, Lancaster, for Improvements in the Manufacture of certain Chemical Agents used in dyeing Cotton, Woollen, &c.

THIS invention consists in manufacturing stannate or stannite of soda or potash in a dry, crystalline or pasty state, and in producing the tin-preparing liquor used for dyeing and printing fabrics (hitherto made by mixing oxy-muriate of tin with dilute caustic soda), by dissolving the same in water.

The following is the mode of manufacturing stannate of soda :— 22 lbs. of caustic soda are first put into an iron crucible, heated to a low red heat by a fire beneath; then, after evaporation has taken place, so as to produce hydrate of soda, 8 lbs. of nitrate of soda and 4 lbs. of common salt are introduced; and when the mixture is at the fluxing heat, 10 lbs. of feathered block-tin are added, and it is stirred with an iron stirrer. The mass now becomes dark-coloured and pasty, and ammonia is given off (the tin decomposing the water of the hydrated soda and part of the nitrate of soda); the stirring is continued, as well as the application of heat, until deflagration takes place, and the mass becomes red-hot and of a pasty consistence. This product is stannate of soda, which, being reduced to powder when cold, is ready for use; or, if it is required to be in a more pure state, it is dissolved and crystallized; or it may be dissolved and evaporated to a pasty state, so dry that no fluid will run from it.

Stannite of soda is made by putting 4 lbs. of common salt, $13\frac{1}{2}$ lbs. of caustic soda, 1 lb. of nitrate of soda, and 4 lbs. of feathered block-tin into a hot iron crucible, over a fire, and stirring and boiling to dryness, the stirring of the dry powder being continued as long as any ammonia is given off; this dry powder is stannite of soda.

To produce the tin-preparing liquor, 3 lbs. of stannate of soda are dissolved in 1 gallon of boiling water, and 3 gallons, or more, of cold

water are added, to bring it to the required strength. The stannite of soda is used in the same way.

The stannate or stannite of potash may be prepared in a similar manner to the stannate or stannite of soda.—Sealed July 8, 1846.

Patent granted to Frederick Bankart, Denmark Hill, Surrey, for Improvements in treating certain Metallic Ores.

This invention relates to all ores containing copper, whether combined with sulphur or not; and consists in adjusting and mixing together the different ores in such a manner, that those ores which contain sulphur in excess may compensate for the deficiency of sulphur in the other ores, and submitting the ores, so adjusted and mixed, to successive roastings and lixiviations, whereby a solution of sulphate of copper is obtained, from which the copper may be precipitated in a refined metallic state.

Various modes of precipitation may be adopted; but the patentee prefers to employ cast or wrought iron plates, keeping the solution at a temperature of from 120° to 150° F., and as nearly as may be of the same strength, by means of a circulating stream of fresh sulphate solution, which, entering at the top, and being conducted by a pipe downwards, tends, by its greater specific gravity, to displace the lighter solution; the latter overflowing is to be returned into the lixiviating vat, to be recharged with sulphate of copper, and this again precipitated, until the refuse liquid becomes a nearly saturated solution of sulphate of iron, when it is set aside to crystallize.—Sealed Aug. 7, 1845.

Patent granted to John Leifchild, Minorities, London, for Improvements in the Manufacture of Blue, to be used as a Substitute for Stone-blue.

This invention consists in combining certain descriptions of blue colour, known as Chinese blue and Turnbull's blue, with oxalic acid, so as to render them suitably soluble in water, in order that the combined matters may be used instead of stone-blue, for colouring linen after washing.

The mode of operating is as follows:—4 parts by weight of Chinese blue, 1 of Turnbull's blue and 1 of oxalic acid are well-mixed together, and boiling water is gradually added until the whole is dissolved; and then to this combination an addition is made of 1 part by measure of the liquid called sulphate of indigo, which is produced by mixing 1 part of indigo with 4 parts of concentrated sulphuric acid, and afterwards neutralizing the excess of acid by means of carbonate of ammonia. The combined liquid, when required for use, is reduced in intensity of colour to the extent desired by the addition of water; it is then ready to be employed for blueing linen after washing, as hitherto practised when stone-blue in water has been used.—Sealed July 8, 1845.

THE CHEMICAL GAZETTE.

No. LXXXIII.—April 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Volatile Acids in Angelica officinalis.

By H. MEYER and Dr. ZENNER.

SOME years ago M. Buchner, Jun. discovered a volatile acid in the root of *Angelica officinalis*, which resembled valerianic acid, and to which he gave the name of angelicic acid. It was said to be of an oily consistence at the ordinary temperature, but to crystallize in large prisms a few degrees above 32° F., to form readily soluble salts with the alkalies and earths, sparingly soluble white precipitates with lead and silver, and a flesh-coloured precipitate with peroxide of iron. It was the authors' intention to submit this acid to a more accurate examination; and they at first followed the mode of preparation described by Buchner, which consists in extracting the root with alcohol, distilling off the latter, and evaporating until the dark brown residue, which possesses an aromatic odour, separates into two layers, both of which have an acid reaction; the upper one was resinous and soluble in alcohol and æther, the lower one brown and soluble in water. The first was collected and washed with water; in this state it forms the so-called *Angelica balsam* of Bucholz and Brandes, and is a semifluid brown mass, which is obtained in large quantity. This resinous substance was boiled with solution of potash (1 part hydrate of potash and 10–12 parts water) in a retort with a recipient until entirely dissolved, in the latter a turbid water collected together with a very small quantity of an essential oil. The residue in the retort was supersaturated on cooling with dilute sulphuric acid, when the resin again separated. After this treatment it dissolved only partially in æther. The liquid smelt very strongly of valerianic acid, and on distillation a strongly acid milky product collected in the receiver, which on being well-cooled with water deposited crystals. An acid oil floated on the surface of the distillate.

To obtain the acids in larger quantity, 50 lbs. of the dried root were boiled with 3–5 lbs. of hydrate of lime and the same quantity of water, the liquid was filtered through linen, and the residue submitted to pressure; the deep brown liquor was evaporated, supersaturated with sulphuric acid and redistilled. A strongly acid turbid water, of an aromatic odour, resembling that of fennel oil, collected in the

receiver, and on its surface floated an acid oil. The residue in the retort consisted of gypsum and extractive matters, and moreover of a brownish resinous substance, soluble in alcohol; the distillate was supersaturated with potash and evaporated, when the peculiar fennel-like odour disappeared, while the liquid gradually acquired a brown colour. The evaporated saline mass was acidified with sulphuric acid and again distilled. On incipient boiling, a very acid turbid fluid passed over, possessing the odour of valerianic acid; it was intermixed with numerous drops of oil, and on well-cooling deposited large white masses of crystals. The distillate was left quiet for several days, when the crystals increased in number, and separated in needles and columns frequently more than an inch long. A small quantity of crystals was likewise obtained from the oil by artificial refrigeration. The oil was then rectified once more along with the aqueous distillate, and removed with a pipette; but the water was saturated with carbonate of barytes and evaporated in the water-bath.

Examination of the Crystalline Substance.—All the crystals obtained according to the above method were washed with a little cold water, and then recrystallized several times from hot water. Their quantity amounted to between 2 to 3 oz. from 50 lbs. of root. The water had a slight acid reaction, and contained a little of both acids in solution; for when shaken with æther, and this poured off and allowed to evaporate in the air, crystals of the angelic acid were obtained mixed with drops of oil.

The angelic acid crystallizes very readily in tolerably transparent colourless crystals, which have an acid reaction and melt at 113° ; but on cooling they solidify in shining masses; it has a peculiar aromatic odour, boils at 374° , and can be distilled without decomposition; in cold water it is very sparingly soluble, but readily so in alcohol and æther, and likewise in oil of turpentine and fatty oils; it forms with bases salts, which, evaporated in the air, very readily part with a large portion of their acid; those with the alkalies and earths are soluble in water, the former likewise in alcohol. The silver salt is also soluble in water and alcohol. For analysis, crystals dried in the air were exposed for a length of time to a temperature of 212° – 230° , then heated to boiling, and the last half of the acid which passed over collected in a separate dried vessel. It yielded—

Carbon	59.432	59.226	59.603	10	=	750	60.0
Hydrogen	8.060	8.012	8.057	8		100	8.0
Oxygen	32.508	32.762	32.340	4		400	32.0

1250

The silver salt was prepared by dissolving oxide of silver in a hot aqueous solution of the acid, and evaporating the slightly acid liquid at a very gentle heat. The angelicate of silver separates in small, generally somewhat grayish-white crystals. Frequently a salt is obtained which crystallizes in laminæ and contains somewhat more silver; indeed, on evaporation some acid constantly passes off along

with the aqueous vapour. The salt was dried over sulphuric acid *in vacuo*, as it loses acid on exposure to heat. It yielded—

Carbon	29.006	29.152	10 =	750.0	28.968
Hydrogen	3.524	3.556	7	87.5	3.379
Oxygen	11.343	11.165	3	300.0	11.587
Oxide of silver	56.127	56.127	1	1451.6	56.066

Atomic weight of the salt found = 2586.28; of the acid, 1134.68.

In the silver salt, 1 equiv. water of the hydrated acid is replaced by 1 equiv. oxide of silver; the formula is consequently $C^{10}H^7O^5 + AgO$.

The lead salt was prepared by dissolving oxide of lead in the acid, filtering and evaporating the acid liquid at a gentle heat. The salt crystallizes easily and in beautifully developed crystals. It has great tendency to become basic, and then crystallizes in laminæ. If the neutral air-dried salt is heated, it cakes together, and gradually melts to a semitransparent mass, whilst a large portion of the acid is expelled. The salt was likewise dried over sulphuric acid *in vacuo*; that for analysis II. was dried between 140° and 158° , because that for I. still contained some water; in this operation however it lost some acid. The numbers obtained were—

	I.	II.			
Carbon	29.365	29.261	10 =	780.0	29.621
Hydrogen	3.664	3.541	7	87.5	3.456
Oxygen	12.022	11.409	3	300.0	11.850
Oxide of lead	54.949	55.789	1	1394.5	55.035

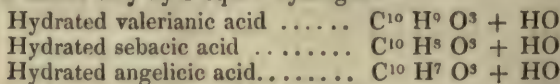
The lime salt was prepared in a similar manner to the lead and silver salt. It is very soluble in water, and crystallizes in shining laminæ. The salt, dried at 212° , does not appear to lose any acid, or the whole of its water of crystallization, like the salts of lead and silver. On analysis it yielded—

Angelicic acid	67.427	67.196	1 =	1137.5	66.19
Water	12.100	12.100	1	356.0	13.09
Lime	20.473	20.704	2	225.0	20.71

The water, saturated with carbonate of barytes, which had been obtained along with the angelicic acid and the volatile (valerianic) acid, left on evaporation a yellowish-white saline mass, which dissolved in alcohol, excepting a residue of a crystalline salt which presented the reactions and the composition of the acetate of barytes. Whether the considerable amount of acetic acid which was obtained from the root exists as such in it, or was formed by the action of the lime, could not be determined.

The portion of the above barytic salt, which dissolved in alcohol, left on evaporation a yellowish salt, which crystallized with great difficulty; it was decomposed by sulphuric acid and submitted to distillation, when it yielded an acid turbid liquid, along with a large quantity of an acid oil, which possessed the odour and other physical properties of valerianic acid. This oil was united with that obtained from the crude distillate, from which the angelicic and

acetic acids had been separated as above described, and the whole employed for the preparation of a zinc salt, which however could not be obtained perfectly pure. The authors found the silver salts to afford a simple and good mode of separating the angelicic and the oily acid. The salts of the latter, which are soluble in water, yield with solutions of silver a white precipitate, very sparingly soluble in water and nearly insoluble in alcohol, which, as above stated, is not the case with the salts of angelicic acid. An ammonia salt was therefore prepared from the impure liquid acid, and this precipitated with a solution of nitrate of silver. The white precipitate was washed several times with water, and then with alcohol, to remove any angelicate of silver. To separate the acid, a portion of the silver salt was decomposed with phosphoric acid, and the valerianic acid obtained rectified over fragments of fused phosphoric acid. Both the silver salt and the acid yielded the known proportions. On comparing the formulæ of valerianic and angelicic acid, it is striking that they differ only by 2 equiv. hydrogen. Angelicic acid is still more closely related in composition to sebacic acid, from which it differs only by 1 equiv. hydrogen:—



Ann. der Chem. und Pharm., lv. p. 317.

The Decomposition of Water by Metals promoted by the Presence of Acids or Salts.

This subject has been extensively investigated by M. Millon, and with highly interesting results. The rapidity of decomposition is sometimes increased a hundredfold, even by a minute quantity of certain salts. Pure zinc in dilute sulphuric acid remains with little or no action; but on adding a small quantity of certain salts decomposition commences at once, and hydrogen is evolved, though differing in the amount of action with the different salts used. Thus, if the action of pure dilute sulphuric acid is represented by 1, that of the bichloride of platinum is 149; of arsenious acid, 123; of sulphate of copper, 45; tartar-emetic, 29; sulphate of silver, 24; and so on with many other salts.

With very dilute muriatic acid (1 to 40 of water), the action is as follows:—for bichloride of platinum, 43; arsenious acid, 38; tartar-emetic, 35.

A solution of oxalic acid has no action on zinc, even when heated; but with a few drops of bichloride of platinum the whole is soon converted into oxalate. The action of acetic acid is hastened by the same chloride, and also of tartaric and citric acids, diluted with 4 or 5 times their weight of water.

This addition of a salt sometimes changes the result. Nitric acid, with $4\frac{1}{2}$ equiv. of water, and diluted with 2 or 3 times its volume of water, poured on iron filings, causes a solution of the iron and the evolution of nitrous acid; but if only one drop of bichloride of pla-

tinum be added, hydrogen is evolved in place of nitrous acid, and protonitrate of iron with nitrate of ammonia is formed.

Bismuth, silver and mercury do not decompose water under any circumstances. Copper, in contact with bichloride of platinum and dilute hydrochloric acid, heated, gives off hydrogen freely; but the same chloride arrests at once the action of nitric acid.

These experiments were extended to other metals with equally important results.—*Comptes Rendus*, July 1845, and Silliman's *Journal*.

On the Products resulting from the Destructive Distillation of the Valerianate of Barytes. By G. CHANCEL.

The salt with which the following experiments were made had been prepared from an acid obtained directly from valerian. It is white, soft to the touch, crystallizes in small transparent shining prisms, and contains 2 equiv. or 9.5 per cent. of water of crystallization; it effloresces by exposure to the air, losing from 2 to 2.5 per cent. water. The salt dissolves readily in water. To test the purity of the acid, it was combined with oxide of silver and analysed, when it yielded exactly the formula of the valerianate of silver, $C^{10}H^9O^3 + AgO$. At 662° the valerianate of barytes loses only its water of crystallization; heated more strongly, it begins to be decomposed, and disengages a gas which burns with a very luminous flame, and at the same time some slightly coloured drops of a powerfully smelling liquid. The decomposition is complete only at a low red heat; the residue is carbonate of barytes, mixed with a small quantity of carbon.

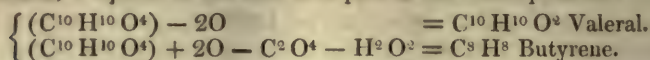
By repeated rectification of the crude distillate, a liquid is finally obtained, which boils at about 230° , and which the author calls *valeral* or *valerianic aldehyde*. It is clear and colourless, very fluid, has a burning taste and a most powerful penetrating odour, is insoluble in water, but soluble in all proportions in alcohol, æther and the essential oils. Its specific gravity at 72° is 0.820.

Valeral is readily inflammable, and burns with a bright blue-fringed flame. Oxidizing agents convert it generally into valerianic acid, as does likewise oxygen in contact with platinum-sponge. Nitric acid yields with it, under violent reaction, a liquid which is denser than water, and in every respect similar to the nitro-butyric acid, on which account the author calls it *nitro-valerianic acid*. In the formation of this body, nitric oxide and a colourless gas are given off, which is easily inflammable and burns with a very bright flame. The analysis of valeral yielded—

Carbon	69.0	69.8	69.5	10	=	750	69.8
Hydrogen	11.6	11.8	11.9	10		125	11.6
Oxygen	18.6	18.4	18.6	2		200	18.6

The specific gravity of the vapour was found to be 2.93; according to calculation it is 2.96. Löwig, who first examined the products of the dry distillation of valerianic acid, states that he obtained pure valeron; but this would require far more carbon (76 per cent.)

than the above analyses show. In the dry distillation of the valerianates, 2 equivs. of the acid take part in the decomposition:—



Valeron is a compound of the two bodies $C^{18} H^{18} O^2 + C^{10} H^{10} O^2 + C^8 H^8$. The gases therefore which are evolved during the dry distillation of the butyrate of barytes are perhaps only butyrene.—*Comptes Rendus*, xxi. p. 905.

On the Freezing of Water by the Air-pump, without the aid of Sulphuric Acid or any other Desiccating Agent. By J. LAWRENCE SMITH.

In attempting to freeze water under the air-pump without the aid of a desiccating agent, the cooling of the water to the point of congelation is prevented by the heat received from the containing vessel. I have lately found that by obviating this difficulty, water may be readily frozen by its own evaporation.

It was first shown by Count Rumford, that water does not wet a sooted surface, but forms in globules like quicksilver. Three drops of water were placed in a sooted watch-glass; the spheroidal globule lay on the soot, exposing a large surface for evaporation, at the same time that the water was insulated from any source of heat. Arranged in this manner and placed under an air-pump, 2 or 3 minutes were sufficient to freeze the water. The glass was sooted over an oil-lamp with great care; the experiment fails if the globule of water touches the glass even by a small point.

In place of the sooted watch-glass, make a shallow cavity in the end of a large cork, and over a lamp burn it, sooting it at the same time. By putting 3 drops of water into the cavity thus prepared, and subjecting it to the action of the air-pump under a pint receiver, the water solidified in $1\frac{1}{2}$ minute; and in $2\frac{3}{4}$ minutes 20 grs. of water congealed, though at 73° F. when introduced. Under a receiver of 3 quarts capacity, 20 grs. of water froze in 4 minutes. I could not succeed in freezing the same amount in the sooted watch-glass.

By placing corks, prepared as above, over a saucer of sulphuric acid, the same results are obtained more rapidly. I put $\frac{1}{2}$ a drm. of water, at 65° F., in each cavity, and exhausted the receiver till the mercurial gauge reached $\frac{4}{10}$ ths of an inch, which was effected in 1 minute. In $1\frac{1}{2}$ minute the water on one cork began to freeze, and in 5 minutes they were all frozen. An ounce of water in a large flat cavity froze in $3\frac{1}{2}$ minutes.

A flat-bottomed porcelain capsule was prepared for an experiment on a large scale, by sooting it in the following manner:—After coating it with soot over a lamp, and allowing it to cool a little, a small quantity of oil of turpentine was carefully poured upon the edge and passed over the entire surface; the vessel was then warmed to drive off the redundant turpentine. The surface was again coated with soot, and again with turpentine, and this process was repeated

a third time; finally, another coating of soot was added, when it was ready for use. 2 oz. of water were placed in this capsule under a receiver, and the air-pump worked for 1 minute. After standing 6 minutes, the surface was frozen.

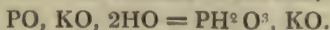
This experiment, as well as similar ones, was attended with violent ebullition on the part of the liquid, throwing the water against the sides of the receiver, which was owing to the rapid formation of vapour on the under surface of the liquid.—Silliman's *Journal*, March 1846.

On the Constitution of the Hypophosphites. By A. WURZ.

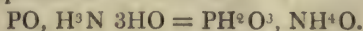
The author prepared almost the whole of these salts, which he analysed, by the double decomposition of soluble sulphates with hypophosphite of barytes; the most economical method of preparing the last-mentioned salt, is to boil a solution of sulphuret of barium with phosphorus, until gas ceases to be evolved. If the ebullition has been long continued, the sulphuret of barium is almost entirely decomposed, and a slight excess only is left, which may be separated by carbonate of lead. Sometimes, however, the excess of sulphuret is more considerable; it is then best separated by cautiously adding small quantities of sulphuric acid to the hot filtered liquor, as long as sulphuretted hydrogen is disengaged. If the liquor becomes acid, it must be neutralized, before evaporation, by a little carbonate of barytes.

Hypophosphite of Potash.—This salt was prepared by the double decomposition of hypophosphite of barytes and sulphate of potash. The aqueous solution was evaporated to dryness, and the residue, treated with hot alcohol, deposited hypophosphite of potash on cooling. The crystals of this salt are hexagonal tables. They are very deliquescent, very soluble in weak alcohol, less so in absolute alcohol, and insoluble in ether. They lose no water at 212° Fahr.

Adopting with M. Pelouze 400 as the atomic weight of phosphorus, M. Wurtz gives as the formula of this salt,

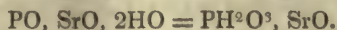


Hypophosphite of Ammonia.—This salt was prepared like the preceding. It crystallizes in large irregular hexagonal laminæ; it is less deliquescent than the salt of potash, and unalterable at 212° Fahr. At about 394° Fahr., it fuses into a transparent liquid without losing water, and becomes a crystalline mass on cooling. It does not decompose under 464° Fahr., at which temperature, like other hypophosphites, it disengages a little water and spontaneously inflammable phosphuretted hydrogen. Its formula, as determined by analysis, appeared to be



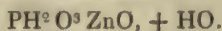
Hypophosphite of Strontia.—This salt was prepared like that of barytes, by boiling a solution of sulphuret of strontium with phosphorus, and decomposing the excess of sulphuret by carbonate of lead, or by sulphuric acid added in sufficient quantity to render the liquid slightly acid. By evaporation the hypophosphite of strontia

crystallizes in the mammillated form by the juxtaposition of small laminæ round a common centre. These crystals are unalterable in the air, and lose no water at 212° . They are very soluble in water, and insoluble in alcohol. The formula of this salt is



Hypophosphite of Magnesia.—This salt was prepared by double decomposition with sulphate of magnesia and hypophosphite of barytes; it crystallizes, as stated by M. H. Rose, in very brilliant regular octahedrons, which effloresce in dry air. The formula of the crystallized salt is $\text{PH}^2\text{O}^3, \text{MgO} + \text{HO} + 5\text{aq}$; of the salt dried at 212° , $\text{PH}^2\text{O}^3 \text{MgO} + \text{HO}$; and lastly, the formula of the salt dried at 360° Fahr., is $\text{PH}^2\text{O}^3, \text{MgO}$.

Hypophosphite of Zinc.—This salt was obtained of two different forms. It crystallizes sometimes in very efflorescent regular octahedrons, and sometimes in small rhombic crystals unalterable in the air. When a moderately concentrated solution of this hypophosphite is submitted to spontaneous evaporation, the first-mentioned crystals are usually formed. They are so efflorescent, that they lose water during pressure between folds of paper, previous to analysis. The formula of the rhombic crystals is



Hypophosphite of Iron.—This salt crystallizes in large green octahedrons, which effloresce by exposure to the air and become a white powder. When exposed to the air, the moist salt absorbs oxygen from it rapidly. The formula of the crystallized salt is $\text{PH}^2\text{O}^3, \text{FeO} + 6\text{HO}$.

Hypophosphite of Chromium.—This salt was prepared by double decomposition by mixing solutions of sulphate of chromium and hypophosphite of barytes. By evaporation there was obtained an amorphous, cracked mass of a very deep green colour. This salt loses water by drying when it has been heated to 392° Fahr.; it is not soluble either in water or dilute acids. The formula of this salt is $2\text{PH}^2\text{O}^3, \text{Cr}^2\text{O}^3 + 4\text{HO}$.

Hypophosphite of Manganese.—The crystals of this salt are of a rose colour, brilliant and unalterable in the air. They do not lose water at 212° Fahr., but at about 302° Fahr. they part with one equivalent. The formula of this salt is $\text{PH}^2\text{O}^3, \text{MnO} + \text{HO}$.

Hypophosphite of Cobalt.—This salt forms large crystals of a deep red colour, which effloresce in the air. At 212° Fahr., they lose six equivalents of water of crystallization, and become a pale rose-red powder. The formula of this salt, which agrees with that of M. H. Rose, is $\text{PH}^2\text{O}^3, \text{CoO} + 6\text{HO}$.

Hypophosphite of Nickel.—The crystals of this salt are regular octahedrons, and smaller than those of hypophosphite of cobalt. When the aqueous solution is evaporated at the temperature of 212° Fahr., it is partially reduced to metallic nickel with the disengagement of hydrogen. This reduction takes place perfectly when the crystals of this salt, broken and slightly moistened, are exposed to the air at

a temperature of 248° Fahr. The formula of this salt is PH^2O^3 , $\text{NiO} + 6\text{HO}$.

Hypophosphite of Copper.—The solution of this salt is readily prepared by decomposing sulphate of copper with hypophosphite of bar-rytes. It is not a permanent salt. At about 140° Fahr. it becomes turbid, and deposits hydrate of copper. By evaporating the solution *in vacuo*, small blue crystals of this salt were once obtained. These crystals decompose quickly, and with projection of the entire mass when heated to 149° Fahr.; and phosphuret of copper is formed. The formula of this salt is PH^2O^3 , CuO .—*Ann. de Ch. et de Phys.*, Fevrier 1846.

ANALYTICAL CHEMISTRY.

New Process for the Detection of Arsenic in Organic Mixtures. By H. LETHEBY, M.B.

THE author found that Reinsch's process was neither certain nor delicate; it was true that the copper would withdraw every and the smallest trace of arsenic; but when this quantity was minute, it was by no means easy to detect it afterwards. The author therefore, reflecting upon these circumstances and upon the exceeding delicacy of Marsh's test, was led to believe that if some other metal were used, which like copper not only had the faculty of withdrawing the poison, but would also serve for the generation of hydrogen, he might be able to combine the advantages of both the tests, and at the same time avoid their impediments. He found that zinc possessed such a property, removing every trace of arsenic from an organic fluid, and forming an alloy from which arseniuretted hydrogen could be developed with the greatest facility. To apply this method:—The organic liquids are to be slightly acidulated with nitric acid, adding about 10 drops to the ounce, filtered, strained through linen or muslin, and introduced into a flask with about 2 drms. of granulated zinc. The whole is kept boiling for half an hour, not too rapidly, and the mixture is kept acid by the occasional addition of a drop or so of nitric acid; during this time the arsenic will be precipitated on the zinc, giving it a grayish-black appearance. The zinc is then removed, and repeatedly washed with boiling water to remove all organic matter. If the substance is solid, as the liver, intestine or muscle, it must be previously cut up into small pieces and placed in a porcelain dish, then covered with a mixture of 2 parts of muriatic to 1 of nitric acid, and evaporated to dryness, taking care that it does not boil very rapidly; thus the tissue will be destroyed and the arsenical compound converted into arsenic acid. The charred mass containing it is broken up, boiled in two or three successive portions of water, filtered, and having ascertained that the mixed liquids are acid, introduced into a flask with the zinc as above.

The second stage of the process consists in introducing the zinc with some dilute sulphuric acid into an apparatus modified from that of Marsh. It differs from the latter in the lower curved portion being again curved in the centre, but in the opposite direction, thus forming an undulating portion consisting of three curves in the same plane, the two lateral of which have the convexity directed downwards, that of the centre being upwards. Near the summit of the longer limb, as usual, there is a bulb; the shorter limb has two bulbs, one large and close to the bottom, the other a little above it; the first serves to hold the zinc, the second to break any bubbles which may arise. The central curve just spoken of, and the convexity of which is directed upwards, serves to prevent the gas from backing and escaping through the longer limb, and to prevent the zinc from falling into the tube below the lowest bulb in the shorter limb; a pointed piece of glass-tubing, loosely fitting the lower part of the shorter limb, should be placed in it. A cap, into which a stop-cock screws, is cemented to the upper part of the shorter limb, and two pieces are to be ground into the upper opening of the stop-cock, and so adapted that they may be removed at pleasure. One of these pieces is a jet for burning the gas; the other, a right-angled tube, to which another of Berlin glass, 6 inches long and $\frac{1}{8}$ th of an inch in bore, can be connected by means of caoutchouc or bladder; to the other end of this another right-angled tube is adapted, and its lower limb made to dip into a solution of nitrate of silver. When used, the arsenicated zinc is introduced into the bulb, the stop-cock screwed on, and the right-angled tube fixed on. Dilute sulphuric acid, of spec. grav. 1080 (1-7), is then added, when the gas is evolved, and must be transmitted slowly through the solution of nitrate of silver until it begins to blacken it; the stop-cock is then turned, the right-angled tube removed, and the jet substituted. The ordinary tests may then be applied.

The solution of nitrate of silver may also be tested by precipitating with slight excess of muriatic acid, gently boiling for a short time and filtering. Evaporate the filtered liquid to dryness, then redissolve the residue in a little distilled water, neutralize with a drop of ammonia, and make it boil so as to expel any excess of the latter. On testing with nitrate of silver, the arseniate is deposited if arsenic had been present; while there is no change, or but a white cloudiness, if it had been antimony or sulphur.

The only impediment the author has found to this process is, that a salt of mercury gives a mercurial coating to the zinc, and thus prevents the deposition of the arsenic, and the subsequent action of sulphuric acid upon it. It must however exist in very considerable quantity to offer any serious impediment.

The fallacies most likely to be met with are antimony and sulphur, both of which give a dark coating to the zinc, and evolve a gas which has the power of blackening the nitrate of silver; but these fallacies are completely guarded against in the subsequent stages of the process.

This test acts in water containing $\frac{1}{200000}$ th part of arsenic, and

it is not difficult to discover the $\frac{1}{200}$ th of a grain even when mixed with many ounces of organic matter, and by careful management it is possible to detect a much smaller quantity.

The principal precautions requisite to be attended to in applying this method are, that the solutions be not boiled too rapidly, that enough zinc be used to precipitate the whole of the arsenic in a thin film, that the suspected fluid be never made so acid as to act upon the zinc and liberate a gas, that the zinc be very carefully washed before being introduced into the hydrogen apparatus, that the reduction-tube contain no lead, and of course that the zinc and sulphuric acid be pure.—*Abstracted from a Pamphlet communicated by the Author.*

CHEMICAL PREPARATIONS.

On an advantageous Method of preparing Chromic Acid, and on a peculiar Behaviour of this Acid towards Sulphuric Acid. By Dr. P. A. BOLLEY.

THE process described by Fritzsche for preparing chromic acid from a hot solution of the bichromate of potash by means of sulphuric acid, is decidedly preferable to every other on account of the large produce. Warrington and Böttger have modified this process, because the product obtained according to Fritzsche's method is not pure, but always contains some sulphate of potash; they recommend mixing a cold saturated solution of the bichromate of potash with 1 or $1\frac{1}{2}$ part of monohydrated sulphuric acid.

The proportion of the sulphuric acid to the bichromate of potash is not stated by Fritzsche; the amount of acid prescribed by Warrington and Böttger is so remarkably great and renders the product so dear, that it is worth while endeavouring to find a process requiring less sulphuric acid.

When 12 to 15 parts by measure of sulphuric acid are prescribed for 10 parts of the solution of the salt saturated at the ordinary temperature, this large amount has certainly some other part to act than the decomposition of the salt, viz. the precipitation of the eliminated chromic acid from its aqueous solution. I endeavoured to separate the two effects, and from the peculiar property which will subsequently be described, I adopted the following process as the best:—

A boiling saturated solution of the bichromate of potash is formed, and during ebullition a weighed quantity of sulphuric acid added to it sufficient to form with the potash bisulphate. The mixture is allowed to cool, when it solidifies for the greater part to a granular red mass. This is not chromic acid, but sulphate of potash, with adherent chromic acid, together with which is formed a concentrated solution of chromic acid, which likewise contains some sulphate of potash. The mass is stirred with a rod to cause the granular part

to subside, and the liquid portion decanted. The residuous mass is agitated with several small quantities of cold water, and what dissolves poured off. In this way there is at last contained in the dish an orange-coloured sulphate of potash with very little chromic acid. Most of the chromic acid is contained in the united solutions.

This process depends on the circumstance, that bisulphate of potash, which is very soluble at a boiling temperature (1 part in $\frac{1}{2}$ water), is dissolved with difficulty at the ordinary temperature, and that cold water mostly removes from it sulphuric acid with scarcely any potash, leaving behind neutral sulphate of potash, while the chromic acid is extremely soluble in the cold water. The concentrated solution of the chromic acid, containing a little sulphate of potash and sulphuric acid, may now be somewhat evaporated, and the chromic acid precipitated from it by the addition of sulphuric acid, without any perceptible traces of the sulphate of potash being thrown down with it; for this salt is readily soluble in the monohydrated sulphuric acid, and still more readily in acid more diluted. The chromic acid is separated from the liquid by draining on a funnel, the neck of which is loosely stopped with fragments of glass, and then dried on porous tiles; by re-solution in water and slow evaporation, it may be obtained perfectly pure in large crystals. In volume there may have been used the same or $1\frac{1}{2}$ time the amount of sulphuric acid, but the solution contains far more chromic acid than with Warington's process. The produce in chromic acid for the same quantity of sulphuric acid is consequently far greater, almost in proportion to the increase of solubility of the potash salt at the ordinary temperature and boiling-point; 1 part by weight of the salt requires at boiling-point nearly 1 part by weight of water, and the solution boils at 103° ; at 18° it requires ten times the amount of water.

If, in this method, sulphuric acid is saved, the chromate of potash, on the contrary, is not wholly turned to account as in the other method; this does not render it less preferable in a pecuniary point of view, for all the residues, both the solid sulphate of potash which is mixed with chromic acid, as well as the acid liquid drained from the chromic acid, may be advantageously employed for the preparation of oxygen. It is only necessary to evaporate the acid somewhat previously, because when very dilute it does not decompose the chromic acid when heated with it. Böttger states that the residuary sulphuric acid may be used for purifying phosphorus from oxide of phosphorus, an application however which is of far less frequent occurrence than the preparation of oxygen.

All the methods above described for preparing chromic acid from its potash salt, readily lead us to believe that the chromic acid is insoluble in monohydrated sulphuric acid, because it is precipitated by it from its aqueous solution; such however is not the case. Sulphuric acid (SO^3 , HO) dissolves considerable quantities of chromic acid at the ordinary temperature, becoming yellow, and finally quite dark brown and opaque. I soon cleared up this apparent contradiction, by adding a few drops of water to the solution of the chromic

acid in the sulphuric acid; the chromic acid immediately separated. Since this proves that the chromic acid is precipitated from its *aqueous solution* by sulphuric acid, but from its *sulphatic solution* by water, then there must exist a proportion between the sulphuric acid and water in which chromic acid is not soluble; to find out this proportion, I made a series of experiments, the result of which was that the amount of water of the sulphuric acid came very near to the formula $\text{SO}^3 \cdot 2\text{HO}$. In fact, if we consider the solution of the chromic acid in monohydrated sulphuric acid as constituted according to the formula $\text{SO}^3, \text{HO} + x\text{CrO}^3$, then CrO^3 is separated on the addition of 1 atom of water.

The author then proceeds to describe a combination of chromic acid with sulphuric acid, which is obtained when the former is gradually conveyed into the latter, and the mixture shaken for some time in a well-stoppered bottle for the complete solution of the chromic acid. After some time no more chromic acid dissolves, and the dark brown fluid, at first of an oily consistence, acquires an ochreous colour and a pasty consistence, and even becomes sometimes granular. Its analysis is difficult, from the avidity with which it imbibes moisture. From the results obtained, however, it would appear to be composed according to the formula $\text{SO}^3 \cdot \text{HO} + \text{CrO}^3$.

In conclusion, the author observes that the solution of chromic acid in monohydrated sulphuric acid is preferable as an oxidizing agent to every other; its action on sugar or alcohol is so complete and quick, that the former, when not added in too large a quantity, may be entirely burnt into carbonic acid and water; while the alcohol, according to the quantity and degree of concentration, may be converted at pleasure either into aldehyde or acetic acid, a change which deserves mention as a very instructive class experiment, because the product of the reduction is immediately visible to the eye, and the product of oxidation readily detected by the organs of smell.—Liebig's *Annalen*, lxi. p. 113.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Production of Artificial Aventurine.

By MM. FREMY and CLÉMANDOT.

ALTHOUGH the manufacture of coloured glass is of recent date in France, it has lately reached such a degree of perfection that the crystal sent out from our works in many cases rivals that manufactured in Bohemia. There is however one product which had hitherto not been made in France, the so-called artificial aventurine, which has hitherto been manufactured only at Venice, the process being kept entirely secret. Beautiful samples of Venetian aventurine are very rare, and fetch enormously high prices.

We have thought it would be interesting to find out the secret of this process; and after numerous experiments performed at the glass-works of Clichy, we have succeeded in obtaining results which, without being perfect in the highest sense of the word, nevertheless lead us to hope that in future aventurine may be manufactured in France.

Chemical analyses, made principally by Wöhler and Barreswil, had shown that the aventurine of Venice consists of a glass holding crystallized metallic copper in suspension. In order therefore to obtain aventurine, it was necessary to cause copper to crystallize in the melted glass, and in such a manner that the crystals of metal remained diffused in the vitreous mass.

After having tried without success the action of various metals on glasses coloured by oxide of copper, we were led to examine the reduction which oxides at the lowest stage of oxidation produce on protoxide of copper, and our attention was principally directed to that which the protoxide of iron (iron-scale) exerts on the protoxide of copper.

We observed that under the influence of heat the iron-scale rapidly reduces the protoxide of copper to the metallic state, becoming itself converted into peroxide, a reaction which appeared highly suitable for the proposed object; it yields, in fact, pure copper, and possesses moreover the advantage of producing a metallic oxide which is soluble in the glass and merely gives it a faint yellowish tint. On heating for 12 hours a mixture of 300 parts of broken glass, 40 parts of protoxide of copper and 80 parts of iron-scale, and then allowing it to cool very slowly, we obtained a vitreous mass containing numerous crystals of metallic copper. The most difficult point therefore in the manufacture of aventurine, which consists in our opinion in producing a glass containing brilliant crystals of copper uniformly diffused throughout its mass, appears to us completely solved.

To convince ourselves of the identity of our aventurine with that which is manufactured at Venice, we examined them comparatively with an excellent microscope, and found that in both the copper was crystallized in regular octahedrons, the copper being in the same state in our aventurine as in that of Venice.—*Comptes Rendus*, Feb. 23, 1846.

• *On the Employment of the Oxalate of Alumina in the Manufacture of Cane and Beet-root Sugar.* By M. MIALHE.

In the course of my researches on digestion and assimilation, I have frequently had occasion to observe the energetic action which the caustic or carbonated alkalies exert on glucose, as well as on cane and beet-root sugar, modified by acids or merely by the simple action of heat—a chemical action to which M. Peligot has directed the special attention of chemists and manufacturers. My observations have led me to reflect on the serious inconveniences which must necessarily result from the use of milk of lime in the clarifica-

tion of sugars. "All the efforts of the manufacturer," says M. Dumas, "should be directed towards improving the mode of clarification, by avoiding as much as possible the use of sulphuric acid, which destroys the crystallizable sugar, and the use of the lime itself, which always imparts a urinous taste to the secondary products, and decreases their value*." But can the employment of lime be suppressed in the clarifying of sugars? I think not. How then shall we proceed?

The first condition is to get rid of all the lime after clarification by means of some chemical agent, which itself is without action on the sugar. Animal charcoal answers but imperfectly; the employment of the oxalate of alumina, which I propose to substitute for it wholly or in part, admits of solving this important problem in a most satisfactory manner.

In explaining the theory of the action of the oxalate of alumina, I may call to mind,—1st, that cane or beet-root sugar, dissolved in lime-water and evaporated to dryness, does not become coloured during evaporation; 2nd, that glucose and cane-sugar, after having experienced the action of acids or an elevated temperature, both acquire under the same circumstances a very marked brownish-red colour. From these facts it follows, that if the cane or beet-root sugar submitted to evaporation contains at the same time glucose, or modified cane-sugar and lime, the product will necessarily be coloured; this is precisely what happens daily in practice. Now I propose to avoid this serious inconvenience by means of the oxalate of alumina. It suffices for this purpose to add to the saccharine solution containing lime a suitable quantity of hydrated oxalate of alumina; the lime is immediately precipitated in the state of oxalate, and the alumina set free subsides in its turn, carrying with it in combination all the colouring matter existing in the mixture—a twofold advantage, the value of which will be readily appreciated.—*Comptes Rendus*, Feb. 16, 1846.

On a Method of ascertaining the Quantity of Gold and Silver consumed in Electro-gilding and Silvering. By MAXIMILIAN DUKE OF LEUCHTENBERG.

The objection of slight durability which has been made to articles gilt by the galvanic process is principally owing to the circumstance that only a very small quantity of gold is allowed to be deposited on the object to be coated. The determination of the amount of precipitated gold by weighing the gilt object is only applicable with small articles, as the scales are not sufficiently accurate for the larger objects. The author therefore advises determining the quantity of precipitated gold from the loss which the solution of chloride of gold employed experiences. For this purpose a decilitre of the liquid is evaporated to dryness, the residue weighed, then 2 grms. of it heated with sulphuric acid, taking care however not to inhale any of the liberated prussic acid, and the heat finally carried to redness. The

* Dumas, *Chimie appliquée aux Arts*, vi. p. 176.

fused mass, consisting of gold and sulphate of potash, is now carefully extracted with water, and the gold remaining in the crucible heated to redness and weighed. After gilding with the solution examined, a decilitre is submitted to the above-described process, and from the difference in the amount of gold in the two liquids, the quantity of precipitated gold is ascertained.

In the process of silvering with the ordinary liquid, which consists of cyanide of silver, cyanide of potassium and chloride of potassium, a decilitre is evaporated as above to dryness, and the residue weighed; 2 grms. of this are then heated to redness, when the cyanide of potassium, chloride of potassium and carbonate of potash fuse, while the cyanide of silver is converted into paracyanide of silver, and is subsequently entirely reduced. After 15 to 20 minutes' ignition, the cold mass is exhausted with water, and the silver remains in the crucible as a spongy mass, so that none is washed away by the water; it is then heated to redness, and weighed. Clay crucibles cannot be employed in determining the silver, as its porous mass imbibes a portion of the fused salt, and so produces a loss in silver.—*Journ. für Prakt. Chem.*, xvi. p. 363.

PROCEEDINGS OF SOCIETIES.

Meeting of the Royal Society.

Thursday, Jan. 29, 1846.

“On the Decomposition and Analysis of the Compounds of Ammonia and Cyanogen.” By Robert Smith, Esq., Ph. D.

This paper is divided into four parts; the first relates to the decomposition of ammonia and its compounds by the compounds of chlorine, and the collection and measurement of the nitrogen gas which is disengaged, the amount of which the author considers as furnishing a ready and accurate mode of estimating the quantity of ammonia in the solution subjected to analysis. The chloride of lime was the salt usually employed for this purpose: this method is regarded by the author as being peculiarly applicable to the analysis of organic substances.

The second part treats of the decomposition and estimation of hydrocyanic acid and its compounds by means of chloride of lime, yielding nitrogen gas and carbonate of lime; a process which occupies but a few seconds. In some cases, the employment of chloride of soda is preferable to that of chloride of lime, on account of the solubility of all the compounds that are formed. The author found the same method applicable also to the analysis of the salts of cyanogen; for the cyanides of the alkalies are decomposed by it as rapidly as the pure acid itself. The ferrocyanides are also very readily decomposed.

The author, in the third part of his paper, relates the results of his trials of the hypochlorites as agents for the decomposition of uric acid, which proved so satisfactory as to induce him to believe that

these salts might be advantageously used as solvents of uric calculi in the living bladder. He also proposes the employment of chloride of lime as a ready and accurate mode of estimating the quantity of nitrogen contained in urine, from the amount of gas disengaged by its action on the nitrogenous compounds. In the last part, the apparatus used in the experiments is described.

Thursday, Feb. 12, 1846.

"On Spontaneous Nitrification." By C. F. Schœnbein, Professor of Chemistry in the University of Bâle.

From various facts adduced by the author, he is led to the conclusion, that during the slow combustion of phosphorus in moist atmospheric air, while ozone is produced, there is also formed a quantity of nitric acid; and that in all cases where both these compound bodies are simultaneously generated, however different may be the concomitant circumstances of the experiment, there is strong reason to suspect that the formation of the one is in some way connected with that of the other.

Chemical Society of London.

March 2, 1846. (The President, Professor Graham, in the Chair.)

"On Crystallography, with a Description of a Goniometer and Crystallonome, or Instrument for studying Crystals in reference to their Gubernatorial Axes," by Dr. Leeson.

The author commences by observing, that discriminative chemical researches have not received that assistance from crystallography which might reasonably be expected from the natural distinction of form peculiar to various different substances.

The particular design of the author's present paper was to introduce greater facility and simplicity in the classification and determination of crystalline forms, both by improved methods of observation, and also by a system of classification founded on the three gubernatorial axes, for the happy discovery of which we are indebted to Weiss, by whom however, as well as by others who have succeeded him, systems have been proposed by no means realizing that simplicity and perfection of which the fundamental principle is believed to be susceptible.

To prove that the nomenclature and classification of the different authors were both confused and complicated, various tables were referred to, showing the systems respectively adopted by them; by referring to which it was apparent that different authors used the same terms for totally different fundamental forms, and also that by many of them terms were employed, which having reference simply to the *number* of planes bounding a given system, were in fact, as subsequently demonstrated, applicable to every class and order, and therefore not *discriminative* of any one in particular.

Any one who may have carefully examined the first crystals depositing from solutions of different substances, will be struck by the general prevalence of the prismatic or hexahedral form, or of some

modification thereof; at the same time he will observe great variety in the *number* of planes bounding many of the crystals. Under the microscope he will not only be struck by the general prevalence of parallelograms, or sections of the prismatic forms, as well as hexagons, triangles, and other sections resulting from hemihedral modifications, but also by the *prima facie* similarity of the sectional forms presented by totally different substances. It is in the discrimination of these forms that the principles of classification now about to be proposed, and the goniometer subsequently described, are peculiarly applicable.

Before describing the system itself, the author requested to explain an instrument which he exhibited, and stated he had contrived some years ago, for the purpose of studying the relative character of crystals derived from different positions and lengths of the three gubernatorial axes, and for which instrument he requested to be allowed to propose the name *crystallonome*.

The author showed with that instrument, that whatever be the length and relative position or inclination of the three axes, a prism or hexahedron must necessarily result from a set of planes terminating the extremities of the respective axes, such planes terminating one axis and being parallel to the other two axes. These planes were represented by a contrivance for attaching pieces of stiff paper or card-board to the extremities of the axes.

The author then showed that an octahedron must necessarily result in every case from a set of planes cutting all three axes, and which octahedron might easily be built up and represented by threads connecting the extremities of all the axes. The construction of other forms was also demonstrated.

The crystallonome, although constructed with only three zones placed at right angles to each other, is nevertheless capable of showing the position of the axes in every class, even where all the axes are oblique. This was illustrated by the instrument itself. It was also shown, that whatever be the class and order of a crystal, there are always two zones in which all three axes will be found.

It having been already stated that the three gubernatorial axes form the basis of the proposed system, it will be evident that the discriminative principles of the system must be dependent on the position and length of the respective axes.

Since the relative position of the axes occasions the greatest difference in the appearance and character of a crystal, it seems natural to take that as determining the class; and we shall find that, as regards this distinctive character, there are but three classes to which the variation of position can give origin, viz.—1st, where all the axes are situated at right angles to each other; 2nd, in which one axis is at right angles to the other two, which are obliquely placed as regards each other, one rectangular axis and two oblique being in fact the same as though we represented it as two rectangular axes and one oblique; 3rd, in which all the axes are oblique to each other.

We have thus three classes, which we term respectively,—1st,

rectangular; 2nd, right oblique; 3rd, oblique; and these we again subdivide into three orders, dependent on the relative length of the axes, viz.—1st, all the axes equal; 2nd, two axes only equal, the third being longer or shorter than the other two; 3rd, all the axes of different lengths. These orders we term,—1st, equiaxial; 2nd, binequiaxial; 3rd, inequiaxial.

With these three classes and three orders we obtain nine distinct crystalline bases, which the author trusts will be found easy to remember and simple to distinguish.

Generally speaking, few substances will be found to crystallize in forms belonging to distinct classes or orders; without however passing any opinion on the subject of dimorphism, the author showed, by reference to the native crystals of sulphur and also those obtained by fusion, that according to the system now proposed sulphur cannot be considered as dimorphous; the native crystals being in fact modifications of the octahedrons or the rectangular inequiaxial system, whilst those of fusion are prisms or hexahedrons belonging to the same system. Both were exhibited to the meeting, and the goniometer subsequently described applied to the measurement of the angles of the crystals of fusion. Whilst a chemical substance usually crystallizes in forms pertaining to the same class and order, it may nevertheless, as has been already shown, assume a great variety of forms if reference be had only to the number of bounding planes, and these forms constitute what may be termed the genera of the author's system, which were shown by reference to diagrams, as also the symbolic notation recommended by the author.

The author concluded by exhibiting his goniometer, consisting of a double refracting prism placed in a vernier revolving round a graduated circle, and applicable either to the microscope or to crystals placed on any convenient stand. He stated, that in most cases of crystallization, particularly under the microscope, some crystals will be observed presenting the prismatic or hexahedral form; and knowing that the gubernatorial axes of any prism must terminate in the centre of the sides of that prism, we are at once directed to the position and length of the axes in any given crystal; whilst by examining the angles formed by the sides of the parallelogram constituting the section of the prism with the goniometer, we may determine the inclination of the several axes.

In all natural octahedrons formed by inaxial planes, the axes will be found, as shown by the crystallonome, by taking the points where four planes meet. Although octahedrons may be mathematically formed by biaxial planes, that is by bending in the sides of the prism, it is believed that such octahedrons do not occur in nature, as it would contradict the general laws of symmetry, inasmuch as whilst the perpendicular axis terminated at the meeting of four planes, the middle and transverse axes would be situated in the centre of an edge bounding two planes; a state of things that could not certainly occur in the regular system; the general condition of natural symmetry being that whatever disposition takes place at any

one extremity of an axis of equal length, the same will take place at its other extremity, and also at the extremities of every other axis of equal length.

"On the Influence exerted by Electricity, Platinum and Silver on the shining of Phosphorus," by Dr. C. F. Schönbein.

The shining of phosphorus in atmospheres containing free oxygen is believed by the author to be intimately connected with the formation of the oxidizing body ozone, and to cease in circumstances in which that substance is no longer produced, as for example at very low temperatures. Since however ozone can be generated, even at these low temperatures, by the agency of electricity, it was thought possible that the electrical brush might confer, while it lasted, the property of shining upon phosphorus rendered dark by cold. Upon trial this was found to be the fact.

In one experiment, at the temperature of 2° R., a piece of phosphorus, placed opposite to the end of a wire from whence a brush of positive electricity was issuing, became brilliantly luminous. The effect was still more striking in the second case, in which the phosphorus was inclosed in a wire-spiral with a projecting point, put in connection with the positive conductor of the machine; a long tail of phosphorescent light was produced, very beautiful in appearance. The shining was interrupted by the cessation of the brush, either immediately or very shortly afterwards. The presence of a minute quantity of olefant gas, vapour of æther, hyponitrous or sulphurous acid, &c., totally annulled the shining of the phosphorus even under the influence of electricity. Platinum black and spongy metallic silver conferred luminosity upon phosphorus in contact with them at 4° and 6° below zero of Reaumur. These bodies are known to produce oxidizing effects.

"On Struvite, a new Mineral," by M. G. L. Ulex.

M. Ulex states that numerous crystals of this substance were found in digging out the ground of St. Nicholas's church at Hamburg. The primary form is the right rhombic prism, measuring $95^{\circ}10'$; the specific gravity is 1.7, harder than talc, and sparingly soluble in water. When heated, they phosphoresce, and before the blowpipe fuse into a colourless glass. Upon analysis M. Ulex found these crystals to consist of $\text{NH}^4\text{O} + \text{MgO}^2 + \text{PO}^5 + 12\text{HO}$; the compound is therefore the ammonio-magnesian phosphate, the same salt which is found in animal concretions and in putrifying urine. This substance was found in a mass of peat-earth mixed with a quantity of cattle-dung, which extends to a depth of 26 feet upon gravel, and here and there a blue earth was present (the earthy phosphate of iron).

M. Ulex then gives an analysis of this earth, considered as the matrix of these crystals, and concludes by speculating upon the cause of the formation of these crystals. It is named Struvite in honour of the minister Von Struve, a well-known mineralogist.

THE CHEMICAL GAZETTE.

No. LXXXIV.—April 15, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Sugar on Tartaric Acid. By M. VOGEL, Jun.

It is a generally known fact that sugar or tartaric acid, exposed to a tolerably moist atmosphere, experience no perceptible alteration; they exert but a feeble attraction for moisture. But the case is very different when a mixture of these two substances is exposed to the air. Whilst this mixture, preserved from the air in a well-stoppered bottle, undergoes no appreciable change, it very soon loses its pulverulent form when placed in a loosely-closed box, and becomes a viscous mass. As soon as it has experienced this alteration, it is no longer possible to obtain crystals of sugar or of tartaric acid from its aqueous solution. These two substances appear to have experienced a mutual decomposition by the exposure of their mixture to the air. The following experiments were undertaken to elucidate the subject.

A mixture of 1 part tartaric acid and 3 parts sugar was exposed to the air in a porcelain crucible. After some days the mixture had already lost its pulverulent form, and it increased daily in weight. The powder successively assumed the form of a viscous mass, which became converted into a transparent liquid, containing the two substances of the mixture in solution.

The mixture, exposed to the air for two months, had become perfectly liquid. The deliquescence proceeds most rapidly when it is exposed on a plate in a cellar, and especially when the sugar and tartaric acid are in equal proportions. After 24 hours, the powder, spread in thin layers, is converted into a perfectly-transparent solution.

Sugar and tartaric acid, exposed separately under the same circumstances to the atmosphere of a cellar, likewise attract, it is true, some moisture, but in a far less degree and less rapidly than when mixed; whence it follows that the affinity of these two substances for the humidity of the atmosphere is increased by their mutual contact. A mixture of 2 oz. of sugar and 1 oz. tartaric acid absorbed more than an ounce of water in becoming liquid.

As I have already stated, it is impossible to extract the sugar or tartaric acid in the crystalline state from the deliquesced mass, for the solution, evaporated to dryness, rapidly re-absorbs water from

the atmosphere. The liquid mass, evaporated to dryness, dissolves entirely in absolute alcohol; but neither the sugar nor the tartaric acid can be separated by crystallization from the alcoholic solution.

The following experiment clearly proves that the tartaric acid has experienced a change by its contact with the sugar. When lime-water is added to the liquified mixture until the acid is perfectly neutralized, but a very small quantity of tartrate of lime is deposited, and the filtered liquid contains a large quantity of a salt of lime in solution. The acid seems therefore to have experienced, by its contact with the sugar, one of those modifications discovered by Fremy, and to have become converted into *tartralic* acid. The liquid neutralized with the lime-water acquires an acid reaction when oxalic acid, not in sufficient quantity to precipitate the whole of the lime, is added to it.

To be certain that the tartaric acid is converted, by its mixture with the sugar, into tartralic acid, it was requisite to separate the two substances contained in the liquefied mixture; this may be done by adding carbonate of barytes to it until it is perfectly neutral, and without raising the temperature. There is formed, in this case, a small quantity of tartrate of baryta, which being insoluble in water remains on the filter, and the filtered liquid contains the sugar with the soluble salt of barytes. When alcohol is added to this solution, a precipitate is formed, which dissolves entirely in a small quantity of water; this aqueous solution becomes turbid when boiled, and deposits tartrate of barytes, which is formed by the elevation of the temperature. The precipitate behaves therefore like a salt of tartralic acid, which is converted at the temperature of boiling water into tartrate of barytes. On decomposing with dilute sulphuric acid the first precipitate separated by the addition of alcohol, we obtain, on the evaporation of the liquid *in vacuo* over sulphuric acid, a viscid liquid, which has all the properties of tartralic acid.

It is very probable that in the tartaric acid syrup of the pharmacopœias this acid likewise exists in the state of *tartralic* acid. If, consequently, cane-sugar is converted by tartaric acid into grape-sugar, a fact which has long been known, it is not the less true that in this reciprocal action the sugar on its side reduces the acid to the state of tartralic acid.

To avoid the objection which might be made, by attributing the more decided affinity of the mixture for water to the greater degree of division in which the tartaric acid exists owing to its mixture with the sugar, I exposed a mixture of the acid and gum-arabic to moist air; but this absorbed no more water than the tartaric acid in the isolated state, and I was able to obtain from it the acid in well-defined crystals by means of alcohol and even by water. Tartaric acid experiences therefore no decomposition when exposed to moist air mixed with gum.—*Journ. de Pharm.*, March 1846.

On the Presence of Hydrosulphuret of Ammonia in Hail.

M. Pelletier, in a letter addressed to the French Academy, states that the hail which fell between the 26th and 27th of January at

Douè-la-Fontaine, diffused a very appreciable odour of sulphuretted hydrogen in places little exposed to drought, and yielded the characteristic black precipitate with acetate of lead; on tritulating the hail-stones with some caustic lime, evolution of ammonia resulted, which was very sensible to the smell, and equally so by its action on moist reddened litmus-paper.—*Comptes Rendus*, March 2, 1846.

On Icica Resin. By F. SCRIBE.

This resin occurred in the collections of the Museum of the Jardin des Plantes, under the name of *Storax de Cayenne*; its appearance however distinguishes it readily from the ordinary storax. The plant producing it is not known. Brongniart derives it from the genus *Icica*, which is widely diffused in Guiana, and belongs to the family of the *Burseraceæ*. This supposition is confirmed by the resemblance of its constituents to another resin which was certainly derived from the genus *Icica*. It forms small opaque granules or masses of a whitish-yellow colour, and is mixed with pieces of bark. Its odour, which is increased by warming or powdering it, is agreeably sweet; it may easily be reduced to a powder, and has a white fracture traversed by yellowish veins. It does not dissolve in water, and yields no volatile substance to it. It dissolves in alcohol with much greater difficulty than all other resins, requiring 55 parts by weight of cold and 15 parts of boiling alcohol, and $3\frac{1}{2}$ parts of oil of turpentine. It consists of three distinct resins, which differ by their solubility and their composition, but are all perfectly neutral. They do not dissolve in alkalies, are not precipitated from the alcoholic solution by lead or silver salts, and do not redden litmus. These resins, of which two are crystallizable, and which the author has named *Breane* and *Icicane*, may be separated from one another by their solubility in alcohol. The *Icica* resin is dissolved in boiling alcohol and filtered while hot, when the *breane* separates in crystals on cooling, while the other two resins remain in solution.

Breane.—After its separation from alcohol, it is recrystallized and dried *in vacuo* at 248° . Its analysis yielded—

Carbon	83.85	83.83	84.12	80 =	84.06
Hydrogen	11.65	11.91	11.87	67	11.73
Oxygen	4.50	4.26	4.0	3	4.21

The resin may be looked upon as the hydrate of a carburetted hydrogen, polymeric with oil of turpentine, $C^{80}H^{64}, 3HO$. The numbers obtained also agree with those of the oil of turpentine. The resin is white, dry to the touch, tasteless, and crystallizes readily in small needles, which are perfectly neutral, burn with a smoky flame, and are insoluble in alkalies and water, and sparingly soluble in alcohol. It melts at 315° ; on cooling, it becomes viscous, and may be drawn out into threads; it subsequently solidifies, and resembles amber. On destructive distillation, it melts, acquires a yellow, then a brown colour, gives off empyreumatic oils, a solid yellow amorphous substance, which is deposited in the neck of the retort, and

leaves a small residue of ash. Concentrated sulphuric acid dissolves it with a red colour without decomposition; nitric acid disengages, on boiling with it, red vapours, and forms a yellow acid substance, which dissolves in nitric acid, but is again precipitated by water. This resin is remarkable from its composition being identical with that of cholesterine, as well as from its relation to the so-called resin of Bonastre in composition and properties, without however being perfectly identical.

Icicane.—The alcoholic ley from which the crystals of breane have subsided still contains the icicane and colophony. On somewhat concentrating the liquid, some impure crystals of breane at first separate, but subsequently crystals of icicane; these, on being washed with alcohol and dried at 248° , yielded on analysis—

Carbon.....	82.11	81.86	160 =	82.12
Hydrogen	11.64	11.50	137	11.71
Oxygen	6.25	6.64	9	6.17

According to the above formula, icicane may be regarded as a combination of breane with the resin which Dumas and Peligot obtained from oil of turpentine on digestion with cold dilute nitric acid, $C^{160}H^{137}O^9 = C^{80}H^{64}, 3HO + C^{80}H^{64}, 6HO$. With the exception of its greater solubility in alcohol, icicane is perfectly similar to breane; it melts at the same temperature, behaves neutral towards vegetable colours, and yields the same products on distillation. More than ten years ago, Boussingault discovered a resin in *Ceroxy-lon andicola*, which had the same composition, and is probably identical with it.

Colophony.—This remains in the alcoholic mother-ley when the two preceding resins have separated by crystallization. It has quite the properties and the composition of ordinary colophony, but differs from it in some measure by its neutrality.—*Ann. de Chim. et de Phys.*, xiii. p. 166.

Reduction of Chromic Acid by Ammonia, Vapour of Alcohol, &c.
By Prof. BÖTTGER.

If crystallized chromic acid, prepared by Warington's method, be placed, in order to obtain it perfectly dry, upon a slightly-baked clay-plate or tile, and covered with a bell-glass, it acquires in this anhydrous state the property of becoming instantly *red-hot* and *reduced* when ammoniacal gas, which has been dehydrated by caustic potash, is suddenly brought into contact with it, nitrogen and watery vapour being evolved, and oxide of chrome, of a beautiful green colour, being left as a residue. This reduction of the dry chromic acid by ammonia has great resemblance to those interesting phenomena of decomposition to which several years ago I directed the attention of chemists*. In the works quoted below, I have stated that when perfectly dry chromic acid is exposed to an atmosphere

* Chem. Gaz., vol. i. p. 328, and Beiträge zur Physiologie und Chemie, heft ii. s. 83.

of the vapour of alcohol, as also of alcohol mixed with the sulphuret of carbon, it becomes deoxidized and intensely red-hot; and that in the one case, the alcohol was partly converted into a fluid containing aldehyde, and in the other, one containing mercaptan. If it be wished to apply this heating to redness of chromic acid, which has been partly deprived of its oxygen by the above vapours, to the collection in somewhat larger quantity of the evolved gaseous products, the so-called ætheric acid apparatus, described and figured in the first part of my 'Beiträge zur Physik und Chemie,' p. 112, may be best used.

For this purpose, an ordinary simple spirit-lamp may be filled with spirit, the fibrous asbestos-wick cut off to about a quarter of an inch above the wick-holder, the wick then spread out, the upper portion being moistened with a few drops of *absolute alcohol*, and finally about as much as can be contained on the end of a knife of the above-mentioned *anhydrous crystallized chromic acid* placed as rapidly as possible upon it. Instantaneously the alcohol inflames, the chromic acid becomes intensely white-hot, and is reduced to oxide of chrome. If the flame of the alcohol be carefully blown out, the newly-formed oxide of chrome *continues to glow* from the continued evaporation of the alcohol, like spongy platinum (apparently however in a much greater degree), until all the alcohol is evaporated, and is converted into the fluid containing aldehyde. In this way, we obtain a Davy's lamp which leaves nothing to be desired. If, in this experiment, instead of using alcohol, we use alcohol mixed with sulphuret of carbon, it is easy, with the use of the above-mentioned ætheric acid apparatus, to obtain a considerable quantity of a fluid smelling of mercaptan, even in a few days. If other readily vaporizable fluids, such as rectified oil of turpentine, nitric æther, naphtha, acetic æther, &c., be subjected to the same procedure, we obtain, exactly as with spongy platinum (instead of the oxide of chrome), the most varied products of decomposition, to which I have already directed attention in the first part of my 'Beiträge,' p. 113, products which deserve more investigation than my leisure permits me to devote to them. To mention an instance:—It might be thought probable that *naphthaline* would be formed by the dehydrogenation of the rectified oil of turpentine in the above proceeding; however, this is not the case; but we obtain a very peculiar transparent odoriferous *liquid*, with the chemical constitution of which I am at present unacquainted, but which is perfectly free from naphthaline. I shall take this opportunity of briefly mentioning some facts lately observed by Dr. Reinsch, which are somewhat related to those above mentioned, with regard to the incandescence of *iron, copper, brass, &c.* in the vapour of alcohol, at the same time modifying them slightly. If Dr. Reinsch is of opinion that the above metals, when heated to a certain point, under favourable circumstances, become red-hot and continue to glow in the vapour of alcohol, I believe that he is in error. According to my observations, the above property cannot be ascribed to the above metals, but only to some of their oxides, as was shown, if I mistake not, by Döbereiner

in the case of peroxide of manganese, oxide of nickel and cobalt. Every one who has performed the experiment exactly as described by the discoverer, must have found that it requires a long time for it to succeed perfectly, for instance, to keep a small coil of iron wire red-hot; and when at last it occurs, on more accurate investigation, it may be seen that it only continues to glow, because its surface is completely metamorphosed, *i. e.* converted into *red oxide*. A coil, which in this manner by long use has become converted superficially in almost its entire extent into peroxide of iron, will exhibit this phenomenon of glowing in an atmosphere of the vapour of alcohol, equally as well as a pure metallic platinum coil; whilst an iron coil, *not coated with the oxide*, cannot be made to glow under any circumstances. How this applies to brass and copper I do not know, as I have not made any experiments on this point; I imagine however that these metals also act in the same manner as iron.—Liebig's *Annalen*, Jan. 1846.

On the Atomic Weight of Chromium. By M. BERLIN.

From the analysis of the acetate of the protoxide of chromium and of the protochloride of chromium, M. Peligot was induced to consider that the atomic weight of chromium hitherto adopted of 351·8 was too high, and that it should be reduced to between 325 and 335. This has led M. Berlin of Stockholm to make a fresh determination of its atomic weight, for which purpose he selected the chromate of silver; this was reduced in a weighed flask with a mixture of muriatic acid and alcohol, the chloride of silver separated by lixiviation from chloride of chromium, the former then dried in a flask, digested with *aqua regia* until it had become snow-white, then fused and weighed. The solution of the chloride of chromium was mixed after evaporation with an excess of ammonia, dried, boiling water poured over it, the precipitated hydrated oxide of chromium collected on a filter, ignited and weighed. Five experiments, performed in the above manner, yielded (supposing $\text{Ag} = 1349\cdot66$ and $\text{Cl} = 443\cdot28$)—

I.	II.	III.	IV.	V.
328·80	328·45	328·83	327·83	328·04

The salt for I. II. III. had been prepared with an excess of chromate of potash from several crystallizations; IV. was precipitated from an excess of nitrate of silver; and for V. bichromate of silver, in tolerably large crystals, was employed.

If, accordingly, we admit the atomic weight of chromium to be 328·39, it follows that there is in—

	Oxide of chromium.	Chromic acid.
Chromium	68·645	52·259
Oxygen	31·355	47·741

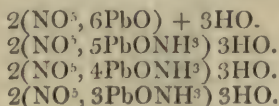
Poggendorff's *Annalen*, No. 2, 1846.

On some new Compounds of Lead. By Mr. CALVERT.

In a previous paper on the action of the fixed alkalies on the hydrated protoxide of lead*, the author described three isomeric states of this oxide—two crystalline, one red, and the other rose-coloured; the third red and amorphous, exhibiting great analogy to minium. The author considers that the colour of minium is not due to the presence of the small proportion of free or combined peroxide of lead which that product contains, but to a molecular change produced under the influence of heat.

On examining the action of ammonia on the hydrated protoxide of lead under nearly similar circumstances, he obtained three greenish-yellow crystalline compounds, which contain oxide of lead, ammonia and water in two different proportions. They are 3PbO , NH^4O and 8PbO , NH^4O . These saline compounds may be regarded as plumbates of the oxide of ammonium, or plumbates of ammonia with 1 equiv. water. The author considers this the first instance of ammonia having been combined with a metallic oxide, causing the latter to act the part of an oxyacid; for, in fact, these ammoniacal compounds contain the equivalent of water met with in the ammoniacal oxyalts.

By acting with ammonia on more or less concentrated solutions of nitrate of lead, the author discovered a series of salts, which acquire great interest from the ammonia occurring in them in a very peculiar state. When these salts, which are for the greater part crystalline, are exposed to a gentle heat, they become yellow, and liberate water and ammonia. If they are now allowed to cool, they again become white; but if heated more strongly, they give off red vapours, and yield as final product beautifully yellow slightly fusible beads of oxide of lead. The author is of opinion that they cannot be considered as double nitrates of lead and ammonia, nor as nitrates of lead with 5 atoms of water of crystallization, 2 of which are replaced by ammonia; but that the following formulæ should be assigned to them, starting with the hydrated hexabasic nitrate of lead:—



These salts, which are called *hydrated ammoniacal nitrates of lead*, are conceived to be nitrates, in which 1 equiv. oxide of lead is gradually replaced by 1 equiv. ammonia, just as in organic chemistry chlorine replaces hydrogen in some substances; or, in other terms, ammonia replaces oxide of lead without the harmony presiding over the arrangement of the other elements of the salt taken as type being in any way changed.

The author has also succeeded in obtaining two salts in which the ammonia has acted, not on the oxide of lead contained in the nitrate,

* Chem. Gaz., vol. i. p. 484.

but on the water of crystallization; for instance, in the hexabasic and tribasic nitrates of lead, 1 or 2 equivs. of water are replaced by 1 or 2 equivs. of ammonia as follows:—

Hydrated tribasic nitrate of lead . . . $2(\text{NO}^3, 3\text{PbO}) 3\text{HO}$.

Hydroammoniacal tribasic nitrate lead $2(\text{NO}^3, 3\text{PbO}) 2\text{HO NH}^4 \text{O}$.

Hydrated hexabasic nitrate of lead . . $2(\text{NO}^3, 6\text{PbO}) 3\text{HO}$.

Hydroammoniacal hexabasic nitrate lead $2(\text{NO}^3, 6\text{PbO}) \text{HO } 2\text{NH}^4 \text{O}$.

These salts, which have all the characters of the preceding ones, are likewise produced under very similar circumstances; and indeed their preparation is a remarkable instance of the influence compounds exert on one another, according to the mode of action and the more or less diluted state of their solution.

On boiling the preceding salts with frequently-renewed solution of ammonia, greenish-yellow crystalline powders were obtained, to which the author assigns the name of *nitrated plumbates of the oxide of ammonium*, with the following formulæ:—

First compound . . . $8\text{PbO}, \text{NH}^4 \text{O} + 2\text{PbO}, \text{NO}^3$.

Second compound . . $8\text{PbO}, \text{NH}^4 \text{O} + 4\text{PbO}, \text{NO}^3$.

Third compound . . . $8\text{PbO}, \text{NH}^4 \text{O} + 6\text{PbO}, \text{NO}^3$.

Fourth compound . . $8\text{PbO}, \text{NH}^4 \text{O} + 8\text{PbO}, \text{NO}^3$.

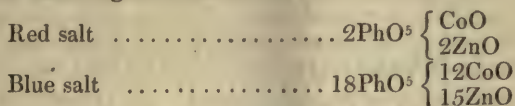
The action of potash on the nitrates of lead is not without interest, as it is impossible to remove the nitric acid, subnitrates being formed, and not pure oxide, as is generally believed; to obtain the pure oxide, it is requisite to pour the solution of the nitrate into a very concentrated solution of potash. Of subnitrates, the author obtained the hydrated tribasic, anhydrous quadribasic, anhydrous pentabasic, hydrated hexabasic, and the hydrated octobasic nitrate of lead.—*Comptes Rendus*, March 16, 1846.

On a Series of Double Phosphates of Zinc and Cobalt.

By M. FLORES DOMONTE.

Struck with the inconveniences which occur in the separation of cobalt from zinc, I endeavoured to ascertain whether a reagent could not be employed for the quantitative separation of these metals, which would precipitate them successively, leaving a sufficient interval between the two precipitations. My expectations have not been realized, the two salts being precipitated confusedly. Nevertheless the experiment led me to the observation of a fact, which is perhaps of some interest. I observed that when a concentrated solution of phosphate of soda was added to a mixture of a salt of zinc and one of cobalt, a magnificent blue, or a rose-coloured salt of an equally pure tint, or a series of other similar salts with intermediate colours, were obtained, according to the temperature or the proportions of the salts employed. They are all insoluble in water, present the same crystalline appearance, and differ only by their tints; they are all brilliant, silky, soft to the touch, resembling thin laminæ of glass or sublimed naphthaline. On analysis I found,—1st, that they all contained zinc, cobalt and phosphoric acid; 2nd, that

these elements enter into the several salts in variable proportions, and that the zinc predominates in the rose-coloured salts and cobalt in the blue: a quantitative analysis which I made of the two extreme compounds, that is to say of the bluest and the reddest salt, yielded the following formulæ:—



Or as a general formula for these two salts, $2\text{PhO}^5, 3\text{MO}$.

Both salts are hydrated; the rose-coloured contains 6 equiv. water for 3 of base; the blue, 54 equiv. for 27 of base; each retain 2 equiv. water for 3 of base, that is to say, 2 equiv. of water for each equiv. of base. This water is partially disengaged at 464° . At this temperature the rose-coloured salt contains 2 equiv. water, the blue salt 18 equiv. The constitution of these double phosphates calls to mind, if I mistake not, that of certain alums, which contain at the same time potash and ammonia in variable proportions.—*Comptes Rendus*, March 9, 1846.

On a Combination of Prussian Blue and Ammonia.

By J. H. MONTRIERS.

An investigation of the double cyanides having led me to re-examine the action of ammonia on prussian blue, I have acquired the conviction that the peroxide of iron, and the ferrocyanide which is formed by the direct action of these two bodies, is only the expression of a final reaction, and that there is formed an intermediate compound, a new prussian blue, in which ammonia is a constituent part. This compound being destroyed by an excess of ammonia, explains how this body has hitherto escaped the attention of chemists.

The best method of preparing the ammoniacal prussian blue is to treat pure protochloride of iron with an excess of solution of ammonia, and to throw the whole upon a filter, taking care that the extremity of the stem dips into a solution of ferrocyanide of potassium. The precipitate which forms is white; it absorbs oxygen from the air and becomes blue, but it is then mixed with sesquioxide of iron, which is formed simultaneously, as in the preparation of basic prussian blue. The whole is then placed in contact for some hours with tartrate of ammonia, maintaining the temperature at 160° to 176° . This salt dissolves entirely the sesquioxide of iron, so that on washing several times with distilled water until no further precipitate results on testing, the blue obtained may be considered as pure.

According to my analysis, this salt is a combination of 3 equiv. ammonia with 1 equiv. ordinary prussian blue; the composition may be represented by the formula $\text{Fe}^3\text{Cy}^9\text{HO} + 3\text{NH}^3$. The property of the ammoniacal prussian blue is that of being more stable than Prussian blue. It is known that the tartrate of ammonia entirely dissolves prussian blue in the cold; the new compound is

not dissolved by this salt, which is a very remarkable property, and furnishes an excellent character for distinguishing the ammoniacal from the ordinary prussian blue.—*Comptes Rendus*, March 9, 1846.

ANALYTICAL CHEMISTRY.

On the Separation of Phosphoric Acid. By Dr. VON KOBELL.

It is well known that the separation of phosphoric acid from magnesia, oxide of cobalt, and especially from oxide of nickel, is both difficult and imperfect according to the methods at present in use. An observation which I had occasion to make in the analysis of a nickel ore, that the arsenic could be far more perfectly separated from the oxide of nickel, by the addition of perchloride of iron to the nitrate or nitromuriatic solution and precipitation with carbonate of lime or carbonate of barytes than by precipitation with sulphuretted hydrogen gas, induced me to make similar experiments with phosphoric acid; which, from this acid being perfectly precipitated by caustic ammonia on a sufficient addition of peroxide of iron or alumina, was expected to yield a most favourable result.

25 grs. of phosphate of magnesia, precipitated in the usual way, well-washed and ignited, were dissolved in muriatic acid, and to this a muriatic solution of 20 grs. of peroxide of iron added, and the whole of the phosphate of iron then precipitated with carbonate of lime. The voluminous precipitate was readily collected on several filters, the lime then precipitated with oxalate of ammonia, and the magnesia again with phosphate of soda and ammonia. The ignited precipitate agreed in weight so closely with the dissolved quantity, that the experiment could be looked upon as perfectly satisfactory; it weighed, for instance, 25.07 grs.

Nitrate of cobalt was now precipitated with phosphate of soda; the precipitate was dissolved in muriatic acid, the requisite quantity of perchloride of iron added to it, and the whole then precipitated with carbonate of lime. The red liquid was evaporated to dryness, and the mass heated to redness; it was then boiled with caustic potash. The ley, examined in the usual manner, exhibited not a trace of phosphoric acid; and, on the other hand, the well-washed precipitate obtained with carbonate of lime presented not a trace of cobalt. The same results were obtained with phosphate of nickel.

This method may therefore be employed in cases similar to the above-mentioned, and is also adapted to the quantitative determination of phosphoric acid in compounds free from iron, as it is only requisite to know exactly the amount of peroxide of iron added to ascertain the amount of phosphoric acid by the increase in weight of the redissolved phosphate of iron precipitated with caustic ammonia. Even with ferruginous ores it may be determined in this way if the peroxide be previously reduced to protoxide by sulphuretted hydro-

gen. But since the precipitate with carbonate of lime is somewhat voluminous according to the quantity employed, it is more advantageous, for the purpose of separation, to treat the phosphate, whose base is insoluble in caustic potash, with caustic potash, and so to extract the greater portion of the phosphoric acid, and then to dissolve the residue along with a small quantity of perchloride of iron, and to precipitate with carbonate of lime or barytes. The same applies to the arseniferous compounds.—*Journ. für Prakt. Chem.*, xxxvi. p. 301.

On a new Method of separating Cobalt from Manganese.
By M. BARRESWIL.

In Rose's work on analytical chemistry, it is stated that the salts of cobalt with a strong acid are imperfectly precipitated by sulphuretted hydrogen, while the salts of manganese are not at all; the new mode of separating these two metals is founded on this fact. Since the cobalt is not precipitated completely from its acid solutions, it will be conceived that it cannot be precipitated but incompletely from neutral solutions; and we are necessarily led to conclude that if it were possible to neutralize the liquid in proportion as it became acid from the elimination of the cobalt, the precipitation would be perfect. Guided by this simple reflection, I ascertained what substance would answer this purpose, and after several experiments I have given the preference to pure artificial carbonate of baryta, which is readily attacked by acid, but not at all by sulphuretted hydrogen; a necessary condition; since were it otherwise, sulphuret of barium would be formed, which, as is well known, precipitates manganese. I may add, that the carbonate of baryta does not produce any precipitate in manganic solutions, as was proved by M. Demarcet, and that baryta is easily removed by means of sulphuric acid, either from the solution or from the precipitate when it is in excess.

The mode of operating is extremely simple. A large excess of carbonate of barytes is added to the solution of cobalt and manganese, and the mixture supersaturated with sulphuretted hydrogen; the cobalt is separated by filtration, while the manganese remains in solution; the analysis is then continued in the usual way.

I hope that this new use of sulphuretted hydrogen will be applicable to the quantitative separation of other metals, such as iron, zinc, nickel, &c., and will render frequent assistance in quantitative analysis. We may now, in fact, separate the metals by means of sulphuretted hydrogen into three series, by acting successively upon an acid solution, a neutral, and lastly upon an alkaline solution.—*Journ. de Pharm.*, March 1846.

On the Quantitative Determination of Arsenic in Alloys and Minerals, by a new Method. By A. LEVOL.

Having observed, in analysing some impure bronzes, that nitric acid yielded with them arseniferous hydrated binoxide of tin and a

solution free from arsenic, I was led to employ oxide of tin as a new means of collecting the arsenic in a medium charged with nitric acid, the utility of which in analysis would be considerable if we possessed a method for separating subsequently the arsenic from the tin.

Of all the means tried for the purpose of solving this latter problem, the one which appeared to me best consists in reducing the arseniferous peroxide of tin by hydrogen. The reduction takes place readily at a dark red heat, and the greater portion of the arsenic is removed by sublimation; nevertheless the tin still contains a certain quantity, which should not be neglected, and which is removed by dissolving it in hydrochloric acid. The arseniated and arseniuretted hydrogen yield on decomposition the whole of the arsenic the tin had retained.

These methods are so convenient that I have employed them for determining the quantity of arsenic frequently contained in the copper and tin of commerce, in bronze, &c.

The best state for employing the tin for the purpose of collecting the arsenic appeared to be that of solution in cold weak nitric acid; the protoxide which is thus formed remaining dissolved, readily comes into contact with the molecules of arsenic; and when the temperature is raised to convert it into the peroxide, it seizes on the arsenic, and carries it down with it.

Arsenic and antimony, oxidized with nitric acid, likewise enter into combination, but the product is not entirely insoluble.—*Comptes Rendus*, March 16, 1846.

On the Detection of Sulphur, and on a Method of distinguishing Sulphurets from Sulphates. By Prof. VON KOBELL.

We possess a very simple method of detecting the sulphur in the sulphurets and sulphates, by fusing the sample with soda upon charcoal before the blowpipe, and thus obtaining a hepar, which on being moistened is readily recognized by means of silver; it is still however uncertain whether the substance contains a sulphuret or sulphate. In many sulphurets, it is true, the evolution of sulphurous acid, on being heated in an open glass tube, decides the question; but in such compounds as Haüyne, Helvine, &c., which contain but a very small quantity of sulphuret, this is impossible. From some experiments which I made on the subject, the following simple process will be found to answer. To distinguish a sulphuret, or a substance containing one, from a sulphate or a sulphatic mixture, the finely-pulverized sample is boiled with caustic potash in a porcelain crucible, and heated till the potash begins to melt, or the sample is fused with hydrate of potash in a platinum spoon before the blowpipe. The mass is then dissolved in a little water and filtered; a bright strip of silver is placed in the solution, and if the sample contained a sulphuret the hepatic reaction is frequently immediately perceptible, but sometimes only after a few hours. With very small quantities, the platinum spoon with the flux may be placed in a little

glass with some water and the silver introduced. The silver is easily restored to brightness by rubbing it with leather and a little caustic lime. It is not necessary to state, that sulphates after such treatment have no reaction on the silver. By this method I was able to distinguish it in Hauyne from Albano, helvine, lapis-lazuli and an artificial ultramarine.—*Journ. für Prakt. Chem.*, xxxvi. p. 308.

PHARMACOLOGY.

Indian Remedies. By WILLIAM WINDER.

ALTHOUGH the Indians, being without the advantages of science to guide them in their choice of remedies in the treatment of disease, derive their principles from mere experience, it is certain that we are indebted to their *Materia Medica* for many valuable articles of a vegetable kind. It is as certain that they are frequently successful in the adaptation of these articles to complaints of a formidable character.

One of the remedies in great use amongst them is the *Geranium maculatum*, which many eminent physicians of the United States rank as one of the most powerful vegetable astringents, being principally composed of *tannin* and *gallic acid*. In the second stage of dysentery and diarrhœa, after evacuants, in hæmorrhages of the alimentary canal, and as a styptic in external bleedings, it rarely fails of giving relief. Its dose is from gr. x. to ʒss. of the powder, or ʒss. to ʒj. of a decoction made with a drachm of the root to half a pint of boiling water. With the Indians it is a favourite external styptic, the dried root being powdered and placed on the mouth of the bleeding vessel. It is also much used by them as a wash in leucorrhœa. Internally, in doses of half a teaspoonful in cold water, they consider it very efficacious in hæmoptysis; and in this opinion they are fully sustained by Thacker, Mease, Bigelow, and others.

The *Xanthoxylum fraxineum*, or Prickly Ash, is one of the most valuable remedies of the Indians for the cure of rheumatism. It is said to resemble guaiacum in its properties, and is much used by the Americans as a remedy in chronic rheumatic complaints, and particularly in cases of a syphilitic taint. Bigelow says he gave the bark of this shrub in doses of 10 and 20 grs. with great advantage.

The *Xanthoriza apifolia* is an excellent tonic. Its composition is principally *resin* and *gum*, and the taste is intensely bitter. The dose is ʒij. of the powdered root. The Indians administer it as a diuretic in dropsy, and also use a cold watery infusion for sore eyes.

A favourite and well-known remedy with the Aborigines is the *Eupatorium perfoliatum*, having the familiar names in the United States of Boneset, Crowwort, Thoroughwort, &c. Its taste is intensely bitter, with a slight astringency, but no acrimony; and its operation is tonic, sudorific, cathartic, according to the mode of its exhibition. It is given in cold infusion in intermittents, continued fevers and inflammatory diseases; to produce vomiting and catharsis,

in *hot* infusion; and as a tonic, in substance. In the United States Pharmacopœia there is an officinal formula.

Infusum Eupatorii.—The natives administer it with good effect in fever, and as a common drink in acute rheumatism, pouring a quart of boiling water on 2 drms. of the leaves, and drinking about 3 oz. three times in the day.

The *Cornus florida*, Dog Wood, is said to differ little in its chemical composition from the Peruvian Bark; and Dr. John Walker states, that of all the indigenous tonics this is the most beneficial in intermittents. 35 grs. of Dog Wood bark are said to be equal to 30 grs. of cinchona. The Indians use a decoction of small branches and buds, in want of appetite and debility of the stomach. It is valued also as a poultice to correct ill-conditioned sores.

The *Polygala Senega* is too well known to need description. It is much used by the Indians, who give it in cold infusion during the remission of fevers, attended with great prostration of strength; and in diseases of the pulmonary organs. They also esteem it highly in female complaints; and in this agree with Dr. Chapman, who considers it the most efficacious emmenagogue, and useful in all forms of amenorrhœa.

It is not a little remarkable, that among all the Indian tribes known to Europeans, the *production of increased perspiration* constitutes one of their principal remedies. A favourite and universal mode of procuring this is by the use of the vapour-bath. The construction of this is similar throughout the different nations of the north-west. Mr. Cormack, in the account of his expedition to discover the Aborigines of Newfoundland, or Red Indians, says that he discovered in a deserted village the remains of a vapour-bath. The method used to raise the steam was by pouring water on large stones made very hot. Over these a hemispherical frame-work, closely-covered with skins, was placed to exclude the external air. The patient then crept in under the skins, with a birch-rind bucket of water, and a small bark dish to pour the water on the stones, and thus enable him to produce the steam at pleasure. He remains so long as the heated rocks retain sufficient heat to raise the vapour, when he retires, wrapped in a robe or blanket, and goes to bed. The bath is principally used in rheumatism, dropsy, and the cold stage of fever. Warm sudorific infusions are taken in the bath; and the debility induced is sometimes so great that the patient faints; which, however, followed by proper treatment, generally has a beneficial effect.

I have said that the Indian is guided by experience in the treatment of disease. For example, when suffering from acidity of the stomach, he takes some of the absorbent earths that are found on the banks of the rivers. Bleeding, in their inflammatory diseases, is also much used. But the simple native of the forest does not employ the former from any knowledge he possesses of the principles of chemistry, nor the latter from any acquaintance with the laws of physiology.

A modern writer states, that in their febrile diseases they make the state of the skin and bowels the guide by which to regulate their

practice. When the skin is moist for a considerable time, and the thirst ceases, they say there is no danger. When the evacuations from the bowels become less offensive and change their colour, the tongue becoming clean, they stop purging and diaphoresis. If there be great debility, they commence giving tonics, which are commonly bitters. Should these induce costiveness or a return of the fever, evacuants are again had recourse to. There is something so rational, and yet so simple, in all this, that I hardly think we should find anything to improve upon it in Sydenham or Cullen; and, as the great Boerhaave tells us, that "simplicity is the seal of truth," probably there is here as much practical unsophisticated truth as will be found in the elaborate treatises of ancient and modern professors.

That the Indians are acquainted with the mode of relieving inward pains by treatment *similar to the Moxa*, is seen by their burning a piece of touchwood over the pained part, and suffering it to produce a blister. They are also aware of the advantage of relaxing the muscles in dislocations; for in cases where they do not succeed readily, they nauseate the patient to a most distressing degree, and then find very little difficulty in reducing the luxation. Tumours and abscesses are allowed to suppurate generally without any application to them. When much inflamed and painful, plasters of bruised herbs or warm fomenting poultices are used. If matter forms, they make an incision for its escape, and continue the poultices to promote the discharge.—*Brit. Amer. Med. Journ.*, Jan. 1846; as inserted in *Monthly Journ. of Med. Science*, April 1846.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a new Method of estimating the Value of Pearlashes by the Natrometer. By ED. PESIER.

THE method which I propose for examining samples of pearlash is founded on the increase in density which the sulphate of soda gives rise to in a pure saturated solution of sulphate of potash, and the mode of appreciation depends on the employment of a peculiar areometer, to which I have given the name of *natrometer*.

This principle is deduced from the following facts founded on experiment:—1st, that a saturated solution of neutral sulphate of potash always possesses a constant density when it is made at the same temperature; 2nd, that the sulphate of soda increases the density of this solution in proportion to its quantity. This is the more perceptible as the solubility of the sulphate of potash is greatly increased when the two salts are present. It is needless to state that the results are the same, whether we take the above salts already formed, or produce them by the decomposition of the carbonates or chlorides with sulphuric acid.

I first thought that in order to obtain a certain degree of accuracy, it was indispensable to combine the whole of the oxide of potassium

with one and the same acid; and this led me to prefer sulphuric acid, the power of which is known. I learned from subsequent researches, that the chloride of potassium, in dissolving in a saturated solution of sulphate of potash, displaced a portion of this salt, and that it did not alter perceptibly the density of the liquid. As much as 50 per cent. must be added, in order to produce an increase equal to that which 3 per cent. of soda would give rise to!

I then endeavoured to ascertain how it acts when soda is joined to the sulphate of potash, and I observed that it rendered the density less than it would have been without its influence. Some syn-
thetical experiments have enabled me to explain this apparent anomaly; chlorine, in the presence of sulphuric acid, potash and soda, combines with the latter base; it is the chloride of sodium, which modifies the solubility of the sulphate of potash, and increases it a little less than does the sulphate of soda; the instrument only indicates 0.125 oxide of sodium when 0.14 to 0.20 is mixed in the state of chloride of potassium with sulphate of potash in excess. If, under these unfavourable and exceptional conditions the error is so slight, the small quantity of chloride which the commercial pearl-ashes contain most frequently permits of our dispensing with its elimination.

These considerations induce me to describe two processes, one of which I consider in the hands of chemists as a method of analysis as perfect, and requiring less time than those hitherto in use; the other, which is but a simplification of the first, is more than sufficient for the purposes of the merchant and manufacturer.

Process of accurate Analysis.—The experiment consists of three distinct operations;—1st, conversion of all the salts into sulphates; 2nd, neutralization and saturation; 3rd, appreciation of the soda by the instrument.

Conversion of the Salts into Sulphates.—I consider it useless to dwell on the manner in which the sample to be examined should be selected. To obtain the mean composition of the potash, the sample should be made up of several small portions taken from different parts of the mass. 50 grms. are weighed off and dissolved in the least quantity of water possible, filtered, and the residue washed several times with fresh water to deprive it of all alkali. Most frequently this filtration may be dispensed with when the potash is of first quality, and leaves but little residue, and it is not desired to obtain minute accuracy. It is only recommended in order to separate the alumina and the lime salts which might by their presence slightly increase the density of the liquid.

The potash being dissolved, it is decomposed by sulphuric acid, and as it is necessary to have an excess in order to expel the hydrochloric acid, all testing is rendered unnecessary by employing a small measure which contains a quantity of sulphuric acid of 1.842 spec. grav., sufficient for every case*. The liquid is then transferred into a

* No fear need be entertained of the dose of acid being somewhat too large, for the chlorides are the more readily decomposed and the fusion is rendered easier. A large excess of sulphuric acid has no other inconvenience than that of requiring more carbonate of potash for neutralization.

porcelain capsule, evaporated, and when it has acquired a somewhat thickish consistence, it should be stirred with a glass rod to prevent any of the mass being thrown out; the heat is then raised until it fuses quietly.

Neutralization and Saturation.—As soon as the crucible is cooled, the mass is dissolved in as little water as possible (less than 300 cubic centimetres), then transferred into a flask with a narrow neck capable of containing 600 grms., and the excess of acid *carefully neutralized* by a concentrated solution of pure carbonate of potash*. As will be conceived, a large quantity of sulphate of potash is deposited in this operation. As soon as the liquid no longer affects the colour of test-paper the addition is discontinued. If too much carbonate of potash were to be employed, this would require a further addition of acid, and it is therefore well to employ weak solutions when the point of neutralization is nearly attained.

It is now necessary to obtain a *saturated* solution of sulphate of potash at the temperature of the atmosphere; this is readily done by immersing the vessel into cold water and frequent agitation. A thermometer placed in this solution indicates when the temperature is nearly the same as that of the air; it is preferable to allow it to become less (even if it should have to be raised some degrees by the hand). The solution is then stirred, and left a few instants to itself, in order that it may become perfectly saturated. This being done, it is filtered into a graduated tube, on which a circular line indicates a capacity of 300 cubic centimetres. If the preceding recommendations have been followed, it will be found that the liquid is not sufficient to occupy this volume. It is completed by washing the deposit of sulphate of potash several times with a saturated solution of the same salt, which it is well to keep, in order to be able to filter immediately, and not to be compelled to wait until saturation has taken place.

Appreciation of the Soda by the Natrometer.—After having mixed the different strata of filtered liquid by agitation, there only remains to immerse the areometer in it. That which I have had constructed possesses two contiguous scales, one of a rose-colour with the degrees of temperature; it indicates at each degree of the Centigrade thermometer the point of density of a saturated solution of pure sulphate of potash. The other represents hundredths of soda; the zeros of the two scales coincide. If we experiment at 0° Cent., the soda will be directly determined; but if we work at 25° C., it is known that the point to which the instrument would sink in the solution of pure sulphate of potash saturated at this degree corresponds to 8 per cent. of soda. It is however there that the zero of the soda scale should be placed; it is easily found by a subtraction.

As experiment has shown that the degrees of soda cannot be equal, that they are smaller in proportion as they indicate more alkali, the observation should be made on the rose-coloured scale,

* This solution is readily prepared by calcining bitartrate of potash on a plate of iron, and exhausting the product with water; the filtered liquid may be immediately employed, but it is more advantageous to concentrate it by evaporation.

which is considered as a measure of equal divisions. From the number found the figure of the temperature at which saturation has been made should be subtracted, and the remainder gives accurately the per-centage of soda. Thus in an operation made at 20° , if the instrument sinks in up to 59, we see on subtracting 20 from 59 that the potash contains $39 : 3 = 13$ per cent. soda.

As the deposit of sulphate of potash may retain some sulphate of soda, it is advisable, in order to obviate all error, to wash it with the saturated solution, and to form with it a second volume of 300 cubic centimetres. The areometer is immersed in it, and the small quantity of alkali which it indicates added to that previously found.

It is scarcely necessary to take into account the fractions of a degree, as 3 degrees of temperature occupy only a space equal to 1 per cent. soda.

For *commercial purposes*, the presence of the chloride is scarcely of sufficient importance to render necessary its being decomposed; the insoluble substances mixed with the pearlash may also be neglected. About 200 grms. of water are agitated with 50 grms. of pearlash in a flask capable of holding 600 grms. water, the solution carefully saturated with sulphuric acid, heated to expel all carbonic acid, allowed to cool, and filtered, the residuary salt washed with a concentrated solution of pure sulphate of potash until 300 cubic centimetres' solution are obtained, into which the natrometer is immersed. If the pearlash is pure, the degree of temperature at which the experiment is made will be found on the red scale of the instrument, beneath the spot where the liquid ascends round the tube; if, on the contrary, it contains soda, some degrees more will be indicated, the number of which, when compared with the adjacent soda-scale, becomes converted into so many parts per cent. of soda; for instance, the experiment made at 12° C., indicates 25° on the natrometer; the 13° in excess are consequently due to the foreign alkali; and on looking for these 13° on the soda-scale, we find that the pearlash contains 4 per cent. soda.

The above method may likewise be employed for determining in a very short time the amount of caustic soda in leys, for instance in those of the soap-manufacturer. For this purpose a certain quantity of the ley is saturated with sulphuric acid, an excess of pulverized sulphate of potash added to it, and the whole well-shaken; upon which 300 cubic centimetres of the solution are measured off, and the natrometer immersed in it. It may be objected to this method, that the soda indicated by the natrometer is not always present in the state of carbonate, but may also be chloride or sulphate. This however is of no consequence, for the object in view is to ascertain the amount of all soda salts in the pearlash.—*Journ. de Pharm.*, viii. p. 249.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

March 16, 1846. (The President, Professor Graham, in the Chair.)

"On Nitraniline, a new Product of Decomposition of Dinitrobenzole," by Drs. Muspratt and Hofmann.

The attempt by the authors to prepare a substitution-compound of aniline, in which the elements of nitrous acid should replace a part of the hydrogen of that body, was, after repeated failures, accomplished; not however by the direct action of nitric acid on aniline, which gave merely nitrate of aniline when the acid was employed cold; or products of decomposition, as carbazotic acid, when heat was applied. Other means, thought likely to yield the body in question, were also unsuccessful. It was at length obtained by the action of sulphuret of ammonium on dinitrobenzole, a product of the long-continued action of nitric acid of great strength upon nitrobenzide. The dinitrobenzole is dissolved in alcohol, saturated with ammoniacal gas, and treated with sulphuretted hydrogen until the conversion is complete and sulphur ceases to be deposited. Hydrochloric acid is then added in excess, and the solution filtered and mixed with potash, which throws down the new substance as a resinous mass of brown colour. It is purified by crystallization from boiling water or alcohol.

Nitraniline contains $C^{12} \left\{ \begin{matrix} H^6 \\ NO^4 \end{matrix} \right\} N$. Its properties are as follows:—It crystallizes from hot water in long yellow needles, is sparingly soluble in the cold, but is dissolved without difficulty by alcohol and æther. The dilute acids also dissolve it, the solutions being precipitated by potash in yellow flakes. It is inodorous in the cold, but when heated exhales an aromatic smell. Nitraniline is fusible at 230° F., and distils without decomposition at a temperature above 540° F. When heated in the air, it takes fire and burns with a smoky flame. In very many other respects the properties of the new substance resemble those of aniline.

The basic powers of nitraniline are exceedingly feeble, and it is utterly destitute of alkaline reaction to the most delicate test-paper. The hydrochlorate, the same salt in combination with bichloride of platinum, the acid oxalate, and some products of decomposition of the base are also described in the present paper.

"On the Blue Compounds of Cyanogen and Iron," by A. W. Williamson, Ph.D.

After referring to the experiments of Gay-Lussac and Berzelius on this subject, the author commences his paper by the examination of the greenish substance left by the action of sulphuric acid on ferrocyanide of potassium, and shows that it may be regarded as ferrocyanide of potassium in which 1 atom of potassium is replaced by iron; it contains 1 proportion of potassium to 2 of iron. By the action of diluted nitric acid and heat, this compound is oxidized, assumes a brilliant violet-blue colour, and may be viewed as ferrid-

cyanide of potassium in which 2 atoms of potassium are replaced by iron; it contains about 1 proportion of potassium to 24 iron. On heating this blue compound with a solution of yellow prussiate of potash, it changes it to ferridecyanide; and if the blue compound be in mass, no trace of yellow prussiate remains behind. The prussian blue prepared from ferridecyanide of potassium and protosulphate of iron is next examined in detail, and also that obtained by the action of oil of vitriol on a solution of ferridecyanide of potassium; the first contains 1 proportion of potassium to 9.3 of iron, the second one of potassium to about 60 of iron. Dr. Williamson considers that the dyeing power of these blues is in the inverse ratio to their quantity of potassium.

Mr. Warren de la Rue described a new substance he had obtained during his investigation of cochineal, in which he has been engaged some time past; it is analogous to the compound obtained lately by Professor Liebig by the action of potash on caseine.

PATENT.

Patent granted to Joseph Cliff, Wortley, York, for Improvements in the Manufacture of Alum and Aluminous Compounds.

THIS invention refers to such fire-clays as contain a great quantity of alumina, especially the "Wortley fire-clay." The improvement consists in extracting the whole or the greater part of the alumina, and converting it into alum and aluminous compounds, and in using the purified clay, either alone or combined with other fire-clay, for making fire-bricks, glass-house pots, crucibles, gas retorts, and similar articles.

The Wortley fire-clay, or any other fire-clay containing alumina in excess, is first ground, then calcined, and afterwards submitted to the action of sulphuric, nitric, muriatic or other acid, more or less diluted with water, and with or without the assistance of heat. The mass being lixiviated with water, the alumina is obtained in solution, and this solution is freed from iron by the employment of prussiate of potash, gallic acid, sulphuretted hydrogen, or some other suitable agent. The patentee now either evaporates the solution by itself, to get the sulphate, nitrate or muriate of alumina according to the acid used; or he mixes the sulphate or muriate of potash, soda or ammonia with the solution, and evaporates and crystallizes the same to obtain the alum salts, and then by roaching, the alum of commerce is formed. After the whole or the greater part of the alumina has been extracted, as above described, the purified and residuary earth may be employed, alone or combined with other clay, in the manufacture of fire-bricks, glass-house pots, crucibles, gas-retorts, and similar articles.—Sealed June 5, 1845.

THE CHEMICAL GAZETTE.

No. LXXXV.—May 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Atomic Weight of Chlorine. By Prof. MARIGNAC.

THE result obtained by M. Gerhardt* differs considerably from that at which I had arrived. He finds that 100 parts chlorate of potash leave on calcination 60·949 chloride, while I found 60·839, agreeing with Berzelius, who long previously had obtained 60·85, and with Pelouze, who found 60·840. It is my intention to show that this difference cannot be owing, as supposed by M. Gerhardt, to a small quantity of chloride of potassium having been carried away in my experiments by the oxygen gas; and I do not think it will be very difficult.

In fact, in all my experiments, besides the stopper of asbestos placed in the neck of the retort to arrest the powder of the chloride, the gas was passed through a U-shaped tube, filled with small fragments of pumice-stone moistened with sulphuric acid, to retain any traces of water arising from an imperfect desiccation of the chlorate of potash. Now, in my last experiments, the salt being perfectly dry, this tube did not increase in weight. It is impossible to admit, in presence of this fact, that any chloride of potassium was carried away; moreover, other experiments prove it still more evidently. I endeavoured to detect the presence of chlorine in the oxygen proceeding from the calcination of the chlorate of potash, either by passing the gas into several washing flasks containing nitrate of silver and sulphurous acid, or by receiving it into a balloon which had been exhausted, and where it remained for 24 hours in contact with ammonia. In both cases I detected the presence of chlorine, but I showed that the quantity was too insignificant to have any influence on the results of the analysis. But by these processes I ought likewise to have collected all the chloride of potassium, which might have been carried away by the oxygen; and as I operated on more than 50 grms. of substance, I ought, according to M. Gerhardt, to have found at least 55 milligrms. of chloride, whilst I did not find one. I do not pretend that that chemist has obtained inaccurate results, but I think it is impossible to suppose that the difference

* The experiments of M. Gerhardt on this subject will be found at p. 38 of the present volume.—Ed. *Chem. Gaz.*

between our results can be owing to any loss of chloride of potassium in my experiments; those of M. Gerhardt not having been described in detail, I cannot pass judgement on them. I will only observe, that he experimented with 4 to 5 grms. substance, whilst I used 60 to 70, which appears to me to diminish considerably all chance of error.

Let us now suppose that the experiments of M. Gerhardt are accurate, and follow out the consequence. In the first place, we find for the equivalent of chloride of potassium the number 936.45. As he has made no other experiment to determine the proportions of chlorine and potassium contained in that salt, we are compelled to calculate them either from the experiments of Berzelius or from mine. Now, according to Berzelius, 100 parts chloride of potassium are equivalent to 192.40 chloride of silver; I found 192.269. From this results, for the equivalent of chloride of silver, one of the two numbers 1801.73 or 1800.50. Now Berzelius found that 100 parts of silver yield 132.75 chloride of silver; I obtained 132.854. I therefore calculate for the equivalent of silver, adopting the numbers of Berzelius, 1357.24; and, according to my own, 1355.25. Chlorine therefore will be 444.49 or 445.25.

Thus, whether we take the analyses of Berzelius or mine, we under no circumstances arrive at the number 450 for the equivalent of chlorine. It is impossible to conceive how M. Gerhardt has obtained this number unless it is founded on analyses, which he has not mentioned in his memoir.

It will perhaps not be useless to offer some observations on the very intimate and carefully determined relations which connect the equivalent of chlorine with that of several other simple bodies. This connection is such, that before pretending to alter the equivalent of that body, and to raise it to 450, it would be requisite to repeat a large number of analyses, the accuracy of which appears to be well-established, but which on this supposition would become quite contradictory.

The equivalent of silver is deduced directly from that of chlorine by the analysis of the chloride of silver; now this analysis is easy; it has been made very frequently, and always with slightly varying results. It is impossible, according to these analyses, to retain 1350 as the equivalent of silver with 450 for chlorine*; the atomic weight of that metal must necessarily be raised, and all the experiments indicate in that case 1370 to 1375; to conform to the views of the partisans of the multiples of hydrogen, we are forced to admit 1375.

The equivalent of carbon is deduced from that of silver by very easy experiments, in which it is impossible to commit any great error. They are based on the decomposition of salts of silver with organic acids. We find very minute researches on this subject in a memoir by Liebig and Redtenbacher on the atomic weight of carbon; they arrived at the same results by the analysis of the acetate, tartrate, paratartrate and malate of silver. I shall confine myself

* This would require that 100 parts silver should yield 133.33 chloride. Berzelius found 132.75, while I obtained 132.85.

here to the acetate of silver, from the ease with which this salt is obtained in a state of perfect purity. 28·8098 grms. acetate of silver yielded 18·6113 silver, or 64·6 per cent. I repeated these experiments two years ago, when engaged in my researches on the atomic weights of several bodies. Never having published the analyses, which I merely communicated at the time to M. Dumas, I will here detail the results.

Having prepared the acetate of silver from pure carbonate of silver and acetic acid, and again purified it by two crystallizations, it was analysed by calcining it in a small porcelain capsule; and I obtained—

Acetate 3·3359 grms. gave	2·1561 silver =	64·633 per cent.
... 3·0527	1·9727	64·621
		Mean = 64·627

This result, corrected for the weight of air displaced in the weighing, gives 64·609, a number extremely near to that obtained by Liebig and Redtenbacher.

Nevertheless, there seemed to me a slight source of error in the process I had followed; in fact, it is impossible to prevent, in this method, some particles of silver being carried away and lost during the decomposition of the salt. To avoid this, I modified the experiment by enclosing the silver salt in a tube of hard glass, through which a current of air was drawn by an aspirator, to complete the combustion of the charcoal after the calcination. On heating first the anterior part of the tube, and advancing the fire gradually to the other extremity, I forced the gases arising from the decomposition of the salt to pass through a long column of reduced but porous silver, so that not a particle of silver could be carried away. By this process I obtained—

Acetate once crystallized ...	24·717 grms. gave	15·983 silver =	64·665 per cent.
Acetate twice crystallized ...	21·202	13·709	64·661
Acetate thrice crystallized ...	31·734	20·521	64·666
Total.....	77·653	50·213	64·664

This process is evidently more accurate than the other, and leads to a somewhat higher proportion of silver. However, it will be seen that whatever experimental result we adopt, the conclusion will always be the same.

If the equivalent of silver is 1375, the equivalent of carbon will be, according to the experiments of Liebig and Redtenbacher, 79, and according to mine, 78·47, numbers which are equally contradicted by the beautiful experiments of Dumas on the atomic weight of carbon. If we start with the number 75 as the equivalent of carbon, which may be considered extremely accurate, we find for the equivalent of silver, according to my experiments, 1349·6. I had arrived at 1349·01 by the simultaneous examination of chlorine, potassium and silver. So perfect an agreement between results obtained by such different processes scarcely admits of our supposing any considerable error in those numbers.

The equivalent of nitrogen is likewise connected with those of silver and chlorine by experiments susceptible of very great precision, so that it would be impossible at present to modify one of those equivalents without first proving by experiments that the analyses hitherto considered as accurate are entirely erroneous. The equivalent of nitrogen is fixed with great precision by the density of the gas; it is 175, or differs very little from it. I adopt the whole number, feeling certain that none of the partisans of the theory of multiples of hydrogen will object to it.

Now if we adopt for one moment the multiples of hydrogen, 1375, 450 and 175 as the atomic weights of silver, chlorine and nitrogen, we arrive at the following results:—100 parts silver should yield 156·36 nitrate; I found by experiment 157·455, and L. Gmelin obtained 157·43 to 157·62. 100 parts silver in solution would be precipitated by 49·09 chloride of ammonium; I obtained 49·556, and M. Pelouze found 49·556 and 49·517. All the results of these experiments are evidently too widely different from the calculated numbers; consequently either all these analyses are erroneous, or the equivalent 450 must be rejected.

I will here mention, in conclusion, some experiments I made with the view of connecting the equivalent of lead with that of chlorine. I never published the results, because they did not agree sufficiently with one another for accurate determinations of atomic weights; I believe however they may be of some interest in this discussion.

If chlorine gas is passed over metallic lead raised to a high temperature, combination takes place with heat and light, and fused chloride of lead is obtained. This method of analysis is very accurate. Some very pure lead was placed in a tube of hard glass, through which a current of chlorine was passed. A stopper of asbestos, placed close to the end, prevented any chloride of lead, volatilized at the moment of combination, being carried away. I obtained in this way the following results:—

Lead 20·506 grms., chloride 27·517 = 134·190 per cent.

... 16·281 ... 21·858 134·255 ...

... 25·454 ... 34·149 134·159 ...

Mean = 134·201 ...

Thus 100 parts of lead combine with 34·241 chlorine; if we calculate thence the equivalent of lead, adopting 443·20 for chlorine, we obtain 1295·87; adopting 450 for chlorine, we should obtain 1315·75.

I likewise attempted to convert a known weight of chloride of lead into chloride of silver by precipitating it with nitrate of silver, and I obtained the following numbers:—

Chloride of lead 12·534 grms., chloride of silver 12·911 = 103·01 p. c.

... 14·052 ... 14·506 103·23 ...

... 25·533 ... 26·399 103·39 ...

Mean = 103·21 ...

This number differs very little from that found by Berzelius, 103·35.

Starting from these results, and adopting the old equivalents of chlorine and silver, we find for lead 1293·27; while if we adopt 450 for chlorine and 1375 for silver, we shall have for lead 1318·24. The equivalent of lead has been determined with very great precision by Berzelius, by the reduction of the oxide of lead by hydrogen, and the number obtained is 1294·5. As will be seen, it agrees very well with my experiments; but it is necessary to discard entirely the equivalent 450 for chlorine.

I do not bring forward the preceding analyses as serving to determine an atomic weight with precision; they differ too much one from another to allow of a mean being taken, but they nevertheless suffice to establish an absolute incompatibility between the equivalent of lead and the equivalent 450 for chlorine; each one, in fact, taken separately, leads to the same result.

The above considerations will probably appear rather long for the purpose of refuting an hypothesis which is not yet supported by a complete series of experiments. I wished however to developpe them, in order to show that, even when a system of experiments apparently irreproachable should lead any chemist again to adopt the equivalent 450 for chlorine, the question would still not be solved; and that, to give weight to such an opinion, he ought to repeat all the experiments above mentioned, and to show what errors could have led to results so different from those which ought to have been obtained according to this hypothesis.—*Bibliothèque Universelle*, Feb. 15, 1846.

On the Solubility of Gypsum in Water and in a Solution of Chloride of Sodium. By M. ANTHON.

The author digested pure artificially-prepared gypsum, at the ordinary temperature, in a closed vessel with distilled water, and in another with a saturated solution of culinary salt. On examination, he obtained from 1000 grms. of the first liquid with chloride of barium 3·1 grms., from the second 11·1 grms. sulphate of baryta. In accordance with this, gypsum dissolves in 438 parts pure water, and in 122 parts solution of chloride of sodium.—*Buch. Rep.*, xli. p. 363.

On the Proportion of Water in the Magnesian Sulphates and Double Sulphates. By THOMAS GRAHAM, F.R.S.

The author denies the accuracy of M. Pierre's experiments, which were given in p. 113 of the present volume, and still adheres to his original view of the constitution of the magnesian sulphates. He has however repeated his experiments.

Of the double sulphate of zinc and potash, 31·46 grs., by drying at 212° for several days, lost 7·75 grs. of water; and by fusion at a heat verging on redness, 0·08 gr. of water additional, making the whole loss 7·83 grs. Hence the composition of the salt, with reference to water, was as follows:—

	Experiment.	Theory of 6HO.	Theory of 7HO (Pierre).
Sulphate of zinc and potash ..	75.11	75.97	72.68
Water	24.89	24.03	27.32
	100.00	100.00	100.00

The experiment obviously indicated 6 and not 7 equiv. of water. The slight excess of 0.86 per cent. of water is not more than is usually found in crystallized salts, arising from the difficulty of divesting them entirely of water mechanically interposed between the plates of the crystals. The peculiarly high disposition of this particular class of salts to retain mechanical water has been noted by Mitscherlich, the author, and almost every one else who has made them the subject of investigation. It has probably been the cause of the error into which M. Pierre has fallen, in over-estimating their proportion of water.

The author also detailed 5 analyses of the double sulphate of copper and potash, lately executed in the laboratory of Prof. Fownes:—

	I.	II.	III.	IV.	V.	Theory of 6HO.	Theory of 7HO (Pierre).
Sulph. of copper and potash ...	74.80	76.00	75.00	74.8	75.6	75.56	72.60
Water	25.20	24.00	25.00	25.2	24.4	24.44	27.40
	100.00	100.00	100.00	100.0	100.0	100.00	100.00

These experiments all concur in proving that 6 equiv. is the proportion of water in the double sulphate of copper and potash, and not 7 equiv.

With reference to the single atom of water strongly retained by the magnesian sulphates, an experiment was made on sulphate of zinc. The crystallized salt, dried for several days at 212° , in the same circumstances as those in which the double sulphate of zinc and potash became anhydrous, still retained water. The heat being continued for 3 or 4 days after the salt ceased to lose weight, it was thereafter found to consist of—

	Experiment.	With 1 equiv. of water.
Sulphate of zinc ..	20.42 89.20	90.03
Water	2.46 10.75	9.97
	22.88 100.00	100.00

It is sufficiently evident therefore that sulphate of zinc, which is admitted by M. Pierre to contain 7 equiv. of water, retains 1 equiv. of water by a stronger affinity than the other 6, contrary to his observation; while, moreover, this strongly retained atom of water is absent in the double sulphate of zinc and potash, the last containing only 6 atoms of water—the experimental data on which the view of the constitution of these salts controverted by him is founded.

On the Composition of Inuline. By A. WOSKRESSENSKY.

Several analyses have already been made to ascertain the composition of inuline; but as it is very readily converted into sugar by

the action of water and other reagents, the results by no means agree. Mulder advances the formula $C^{12}H^{10}O^{10}$ for the inuline obtained from the root of *Taraxacum officinale* and *Inula Helenium*; that from the bulbs of dahlias yielded a somewhat different result. Croockewit therefore supposes that the inuline varies in composition according as it is obtained from different plants, and according to the mode of preparation. In his investigation on inuline, which is said to be far more widely diffused than starch, M. Woskressensky has found that inuline may be prepared of constant composition, and that it contains a far greater amount of carbon and hydrogen than hitherto supposed. To prepare the inuline, the roots of chickory were boiled for a short time with water, filtered hot, and the solution treated with acetate of lead. The filtered liquid was freed from the excess of lead by sulphuretted hydrogen, and quickly evaporated until a pellicle formed on the surface. The inuline, which had subsided on cooling in the form of a powder, was again dissolved in a little water, and precipitated from the solution by strong spirit, as a delicate white powder resembling starch-flour. On analysis it yielded the following results:—

Carbon.	52.373	52.159	24 =	52.409
Hydrogen ..	6.886	6.849	19	6.893
Oxygen	40.741	40.698	14	40.698

As this analysis differs from those of Mulder, the author prepared some inuline from those plants which had been previously used for the purpose. He obtained, by the above-mentioned process, a quantity of inuline from *Radix tarax.*; but it was still impure from a brown colouring substance, and had therefore to be dissolved several times, and again precipitated by strong spirit. On analysis, the author obtained 49.594 per cent. C, 6.865 H, and 43.541 O. The amount of water agrees accurately with the above formula; the loss in carbon may be explained from an oxidation of the inuline occurring in the several re-solutions. To show how rapidly oxidation takes place, a portion was dissolved in water, and digested for $1\frac{1}{2}$ hour. On the addition of spirit, but a small part of the inuline employed was separated undecomposed; most of it remained in solution, and on evaporating the liquid a sweet gummy mass was obtained, which would probably have yielded on analysis the same numbers Mulder obtained.—*Bulletin de l'Acad. de St. Péters.*, v. No. iii. p. 36.

On the Formation of Urethane by the Action of Gaseous Chloride of Cyanogen on Alcohol. By AD. WURTZ.

It is known that the chloride of cyanogen is very soluble in alcohol. If this solution be preserved for some time, it gradually loses its irritating odour, and small white crystals of chloride of ammonium are deposited on the sides of the vessel. This decomposition is favoured by solar light or a moderate heat. Under these circumstances the elements of the chloride of cyanogen act on those of the

alcohol, giving rise to various products, among which I shall first point out hydrochloric æther and urethane.

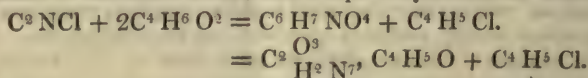
To effect this reaction, it suffices to expose the alcoholic solution of the chloride of cyanogen for some days to the sun, or to heat it for some hours in the water-bath, in a balloon with a long neck, the extremity of which is sealed before the lamp. A strong balloon should be selected, the capacity of which should be double that of the volume of liquid to be introduced. After some hours the balloon is allowed to cool, and the liquid separated from the deposit of sal-ammoniac which has formed submitted to distillation. This liquid begins boiling a little above 122° F.; but on continuing the distillation, the boiling-point very soon rises. If the first portions which pass over are collected in a cool receiver, a layer separates of a very volatile liquid, which begins to boil a little above 68° , and burns with a white flame fringed with green. This liquid consists principally of hydrochloric æther.

After the separation of this æther, the boiling-point keeps for a long time at 176° ; at the end however it gradually rises, and a solid substance, perfectly white, and forming large laminated crystals, condenses in the recipient and in the neck of the retort. This substance begins to boil at about 356° , and distils without alteration; it is soluble in water, alcohol and æther, and is characterized by the remarkable tendency to form crystals of great beauty. It yielded, on analysis, the following results:—

Carbon	40·03	} The formula $C^6 H^7 NO^4$ requires {	40·37
Hydrogen	7·84		7·84

This substance evidently possesses the composition and properties of urethane discovered by M. Dumas twelve years ago, in acting with ammonia on chloroxycarbonic æther. To place this beyond all doubt, I took the density of the vapour of the substance, and obtained the number 3·13; M. Dumas found 3·14.

The reaction which gives rise to the urethane, under the conditions above described, is readily conceivable. 1 equiv. chloride of cyanogen, acting on the elements of 2 equiv. alcohol, yields 1 equiv. urethane or carbamic æther, and 1 equiv. hydrochloric æther:—



Besides these products, there is also formed, by a secondary reaction, a certain quantity of chloride of ammonium. The formation of this body, due to the complete decomposition of the chloride of cyanogen, may be conceived on admitting the simultaneous formation of carbonic æther:—

$$C^3 NCl + 2(C^4 H^5 O, HO) + 2HO = 2(CO^2, C^4 H^5 O) + H^4 NCl.$$

I must however state that hitherto I have not succeeded in detecting the presence of carbonic æther in the products of this reaction.

MM. Wöhler and Liebig announced, some months ago*, that by

* Chem. Gaz., vol. iii. p. 418.

passing the vapour of hydrated cyanic acid into alcohol or æther, there is obtained, besides the cyanuric æther, a fusible volatile substance, crystallizing in transparent laminæ, which dissolve in water, alcohol and æther, and the composition of which is expressed by the formula $CyO, AeO + 2Aq$. This substance would, according to MM. Wöhler and Liebig, be cyanic æther combined with 2 atoms of water.

The preceding formula is identical with that of urethane, and the hydrated cyanic æther is singularly related by its properties and its mode of formation to carbamic æther or urethane. If, as I think, these two substances are identical, this circumstance, in making known to us a remarkable decomposition of the hydrated cyanic acid, can only add further interest to the observations of MM. Wöhler and Liebig.—*Comptes Rendus*, March 16, 1846.

On the Extractives of the Urine. By Prof. SCHERER.

Under this title a mixture of substances has long been included, comprising the mass, partly soluble in alcohol partly in water, remaining after the estimation and separation of the characteristic ingredients of this secretion, viz. the urea, uric acid and the salts. It was evidently a mixture of different substances, some of which were organic, others inorganic. When Pettenkofer undertook his investigation of the peculiar nitrogenous substance in the extractives of the urine, which forms with the oxide of zinc a salt resembling the lactate*, I had already commenced the study of the remaining parts of this extractive matter, especially the colouring principles of the urine, which, as I had ascertained from previous experiments, form the greater part of the so-called extractive matters. The partial decomposition of these substances, on evaporating the urine to separate them according to Berzelius's method, prevented my obtaining any certain results by that process; moreover, separation by solvents, as æther, alcohol and water, depends rather upon the presence or absence of free acid, &c., than upon any difference in the substances themselves. Although it was not possible for me to obtain these matters in exactly the same condition as that in which they existed in the urine, still I consider myself justified in supposing that I have obtained at least approximative results; results which likewise afford proof of the physiological and pathological relations of the organism, inasmuch as all the bodies which were examined were treated in the same manner, and yet constantly varied in the above relations according to a definite rule.

The methods of obtaining these substances were in general as follows:—

1. Fresh urine, passed at various times of the day, was collected, and first treated with solution of nitrate of baryta, to separate the sulphuric acid, part of the phosphoric acid and the uric acid, and filtered from the precipitate, which also contained vesical mucus.

2. The filtered solution was treated with neutral acetate of lead

* Chem. Gaz., vol. iii. p. 125.

until it ceased to yield a precipitate. The coloured precipitate thus formed was filtered and washed.

3. The filtered liquid, which was still somewhat coloured, was now wholly precipitated by basic acetate of lead, and again yielded a copious precipitate, which was however less coloured. This was also filtered and washed.

4. The remaining liquid is now perfectly colourless, and contains the urea, the excess of the barytic and lead salts, and when considerably concentrated by evaporation exhibits some colour.

The first precipitate consists of sulphate, phosphate, urate, and frequently carbonate of baryta; also vesical mucus and biliary colouring matter, if any existed in the urine. In the latter case the precipitate is of a pale bluish or green colour, according to the quantity of the colouring matter present. Distinct traces of the biliary colouring matter were recognised by mixing and warming the precipitate with muriatic acid and alcohol, even in the urine of healthy individuals, especially in the summer. It colours the alcohol green, and the colouring matter may be obtained in the solid state, by evaporating the alcohol and washing the residue with water. When dissolved in water with a drop of solution of potash, it yields the characteristic alteration of colour upon the addition of nitric acid.

The second precipitate, which is most coloured, contains chloride of lead, as also the greater part of the colouring extractive matter in combination with oxide of lead. It is best separated by heating the precipitate with muriatic acid and alcohol. It colours the alcohol red or blackish-brown, according to the nature of the colouring substance and the degree of concentration of the solution, especially if filtered when cold from the chloride of lead, which is insoluble in the alcohol. If the alcoholic solution is now evaporated in the water-bath in shallow vessels as rapidly as possible, a dark brown or black smeary mass is left, from which the muriatic acid may be readily separated by washing with cold water. The water first used dissolves a little of the colouring matter on account of the acid present, but the greater part of it remains as a blackish-brown substance, which is readily pulverized when dried. Its colour varies according to the nature of the substance and the individual relations, from a bright to a blackish-brown colour; and if the lead salt was free from foreign substances, it yields a barely appreciable trace of ash; it is almost insoluble in cold water, somewhat more soluble in hot, and readily so in caustic and carbonated alkalies; also in alcohol, especially when free acid is present. It is less soluble in alcohol when containing caustic or carbonated alkalies. It burns with a peculiar odour, which is very different from that of incinerated urine, more resembling that of humine, to which it is very similar in many of its properties.

The third precipitate, which is less coloured than the last, is at first amorphous, but soon acquires a crystalline aspect from the basic chloride of lead present. When treated in the same manner as the last described, it usually yields a smaller quantity of the colouring extractive matter, and its powder is of a somewhat paler colour.

This difference of colour corresponds, as we shall show presently, to a difference in its elementary composition.

The remaining fluid (4), after the separation of the baryta and lead compounds by means of sulphuric acid and concentration, when the acetic acid escapes, forms a yellowish syrupy mass, from which part of the urea crystallizes as nitrate; the greater part however has become converted into ammoniacal salts. Lactic acid cannot be detected in it.

The urine, of both healthy individuals and those suffering from various diseases, was treated as described, and the substances obtained were subjected to elementary analysis. As they appear to have most analogy, both in general properties and in relative composition, to colouring matters, especially that of the bile*, I consider myself justified in calling them the *colouring matter of the urine*.

I. Urinary colouring matter of a healthy individual, æt. 30; urine, amber yellow.

a. The precipitate with neutral acetate of lead yielded—

	A.	B.
Carbon†	61.312	61.440
Hydrogen‡	6.181	6.020
Nitrogen	7.032	7.032
Oxygen	25.475	25.508

B. was obtained a month subsequently to A. from the same individual.

b. The precipitate with the basic acetate yielded—

Carbon	56.65
Hydrogen	4.10
Nitrogen	6.25
Oxygen	33.00

II. Colouring matter of the urine of the same individual, after the daily consumption of cod-liver oil for 3 weeks, on account of its affording a more highly carbonaceous matter for respiration.

a. The precipitate with neutral acetate of lead yielded—

Carbon	61.99
Hydrogen	6.32

b. With basic—

Carbon	57.22
Hydrogen	5.46

III. Colouring matter from a dark-coloured urine, in a case of severe hectic fever, with disturbance of the respiratory functions, gave—

a. Precipitate with the neutral acetate—

Carbon	65.25
Hydrogen	6.59
Nitrogen	6.79
Oxygen	21.37

* Chem. Gaz., vol. iii, p. 207.

† C = 75.0.

‡ H = 12.5.

b. With the basic—

Carbon.....	58·81
Hydrogen	5·84

IV. From a dark urine, abounding in uric acid, from a case of disease of the liver, with ascites, scirrhus mesentery, and hectic fever.

a. Precipitate with the neutral acetate—

Carbon.....	65·76
Hydrogen	6·01

V. Colouring matter from icteric urine, after the separation of the biliary colouring matter.

a. With neutral acetate of lead—

Carbon.....	64·99
Hydrogen	7·00

b. With the basic acetate—

Carbon.....	60·19
Hydrogen	5·66

VI. Colouring matter in two cases of typhus. The urine was turbid, slightly acid, and of a deep red colour.

a. Precipitate with neutral acetate of lead—

1. Carbon.....	64·43
Hydrogen	6·30

2. From another patient—

Carbon.....	62·80
Hydrogen	6·39

b. Precipitate with the basic acetate (from the same patient as 1.)—

Carbon.....	58·01
Hydrogen	5·95

From these analyses it is evident that the colouring matter of the urine is not secreted of constant composition like the urea, uric acid, and the other constituents of this secretion, but as a substance of variable composition, and in a progressive state of oxidation. In a state of health, and when the functions of the organism are normal, it contains less carbon and hydrogen than in those conditions where, in relation to the consumption of matter, an increase in oxidation by the lungs and skin, or the separation of the above elements by the liver does not ensue. Hence, under such circumstances, the kidneys play the part of freeing the organism from this excess of carbon and hydrogen. Moreover, that portion of the colouring matter which contains most carbon and hydrogen is precipitated by neutral acetate of lead, and that which contains less by the basic salt. Further experiments showed that the whole might be precipitated by the basic acetate. It appears to me that the quantity of the colouring matter obtained by precipitation with the neutral lead salt is less in those cases where the colouring matter is more highly oxidized than in cases where the reverse holds good.

The following comparative experiments show that there is an absolutely larger quantity of carbon and hydrogen in the total amount of colouring matter in the above-mentioned diseased conditions, and not a compensation by relatively greater quantities of colouring matter abounding in carbon and hydrogen. The urine of a healthy individual, and of one suffering from disturbance of the respiratory function, which was caused by the pressure of an effusion preventing the free expansion of the lungs, and in whom there were slight symptoms of fever, was treated as above, first with the barytic salt, and then the whole of the colouring matter precipitated by neutral and basic acetate of lead. The whole precipitate in each urine was then treated as above with muriatic acid and alcohol, and the colouring substance thus obtained analysed:—

I. The healthy individual.		II. The diseased patient.	
Carbon	 58.43		61.65
Hydrogen	 5.16		5.60
Nitrogen	 8.83		7.29
Oxygen	 27.58		25.46

Notwithstanding the colouring matter can be separated by the above lead salts into one portion abounding in carbon and hydrogen, and another containing less, another portion of it may be obtained directly from many urines in the following manner:—If the colouring matter exists in the urine in the state of low oxidation, as for instance was the case in IV., the least oxidized part of it may be very readily obtained by boiling the urine, and then adding concentrated muriatic acid. Urine thus treated acquires a dark colour; and if it contain the colouring matter in a low state of oxidation, on cooling it deposits a tolerable quantity of it, as well as the crystalline uric acid as a dark brown, sometimes bluish powder. It dissolves easily in alcohol, and may be separated by it from the uric acid. The urine IV., when thus treated, assumed a violet colour, and on cooling a dark blue powder subsided, which when dried had a cupreous lustre like indigo, and dissolved with a splendid violet colour in alcohol. On evaporating the alcohol, and subjecting the remaining substance to elementary analysis, it yielded—

Carbon	 66.99
Hydrogen	 5.95
Nitrogen	 7.12
Oxygen	 19.94

When this urine was further evaporated, after the subsidence of this colouring substance, a large quantity of a dark brown colouring matter subsided, which also readily dissolved in alcohol.

The colouring matter, separated from another urine treated in the same way, yielded—

Carbon	 65.51
Hydrogen	 7.45
Nitrogen	 7.08
Oxygen	 19.96

This property of the colouring substance, which abounds in carbon, may be well used, in qualitative examinations of pathological urines, to ascertain readily the kind of colouring matter present, and the greater or less amount of carbon it contains; for the darker the colour assumed by the urine on boiling for a short time in a test-tube with muriatic acid, and the greater the amount of blackish-brown colouring matter which subsides on cooling; the more of it it contains and the more the colouring matter abounds in carbon. The colouring matter of the urine gradually becomes oxidized by the continued action of the air, and the carbon and hydrogen it contains become diminished, just as occurs with the biliary colouring matter*. A portion of the colouring matter III., after long treatment with muriatic acid, yielded,—carbon, 62·51; hydrogen, 5·79. The colouring matter also becomes considerably altered by the mere evaporation of the urine, without the addition of any acid. A quantity of the urine VI. 1, which when treated as above had yielded 64·43 per cent. carbon and 6·30 per cent. hydrogen, was retained for several days at a temperature of 167°–190° F., the water lost by evaporation being replaced. On precipitation with neutral acetate of lead, and decomposing the lead-compound with alcohol and muriatic acid, it yielded,—carbon, 58·63; hydrogen, 5·52.

A quantity of this colouring extractive matter was obtained pure in the manner above described, and treated with sulphuric acid, according to the method of Heintz and Ragsky for estimating the urea. It yielded 18·2 per cent. sulphate of ammonia, or 3·91 per cent. of nitrogen.

Scherer considers it probable that both the colouring matter of the urine and that of the bile are formed from the hæmatine of the blood, whilst the other constituents of these fluids are formed from the so-called proteine compounds of the blood and the organs. This is rendered more clear by the following comparison :—

	Hæmatine (Mulder).	Biliary colouring matter (Scherer).	Colouring matter of urine (Scherer).
Carbon	70·49	68·19	58·43
Hydrogen	5·76	7·47	5·16
Nitrogen	11·16	7·07	8·83
Oxygen	12·59	17·26	27·58

The colouring matter of the urine appears to leave the body in a somewhat less oxidized state after the continued use of a large quantity of food abounding in carbon. Similar relations appear to exist in the formation of the different colouring matters of the urine, to those in the formation of uric acid and urea. We also here find that when the metamorphosis increases, and when the use of organic matter is increased, uric acid, which abounds in carbon, appears, if the functions of respiration and the action of the liver are not proportionately increased. This analogy with the process of formation of uric acid is also evident, from the circumstance that usually the colouring matter of urine abounding in carbon contains excess of carbon itself.—Liebig's *Annalen*, Feb. 1846.

* Chem. Gaz., vol. iii. p. 207.

The Copper Sheathing of Vessels preserved by Chalk.

At a recent meeting of the Asiatic Society of Bengal, the Presiding Member, Charles Hufnagle, Esq., exhibited the curious piece of sheet copper forming the subject of the following memorandum, on which was clearly to be read the words *two foot* in chalk coloured by a thin oxidation of copper, but having distinctly preserved the copper below it from further wear, as stated in the note:—"This copper was placed upon the steamer Hindoostan in England, and since it was there fastened the ship has passed over about 100,000 miles. You will perceive that a *chalk mark* made upon the copper still remains! and the portion of copper under this chalk mark is of *the original thickness*, while the friction, &c. has worn away every other part of its surface. Since this interesting discovery the owners of the ship *Æneas* have chalked over the whole of her copper with the hope of thus preserving it."

On the Solubility of Fluoride of Calcium in Water, and its Relation to the Occurrence of Fluorine in Minerals, and in Recent and Fossil Plants and Animals. By GEORGE WILSON, M.D., F.R.S.E.*

After a preliminary reference to the existence of fluorine in recent and fossil bones, Dr. Wilson stated that he had made a series of experiments with a view to discover what solvent carried fluoride of calcium into the tissues of plants and animals.

His first trials were made with carbonic acid, which was passed in a current through water containing pure fluor-spar in fine powder suspended in it. The fluor-spar was, by this treatment, dissolved, yielding a solution which precipitated oxalate of ammonia, and when evaporated left a residue, which on being treated with sulphuric acid gave off hydrofluoric acid. The author was inclined, in consequence, to suppose that carbonic acid conferred upon water the power of dissolving fluoride of calcium; but on observing that, long after the whole of that gas had been expelled by warming the liquid, the latter remained untroubled, he became satisfied that water alone can dissolve fluoride of calcium, contrary to the universal statement of writers on chemistry.

On prosecuting the inquiry, he found that water at 212° dissolved more of the fluor-spar than water at 60° ; but he has not yet ascertained the proportion taken up by that liquid at either temperature.

The aqueous solution of fluoride of calcium was found to give with salts of baryta a precipitate, which required a large addition of hydrochloric and nitric acid to dissolve it.

The author pointed out the difficulty which must in consequence occur in distinguishing between fluorides and sulphates, and suggested that fluorides may have been mistaken for sulphates in the analysis of mineral waters. He referred also to the objection which

* Being an extract of a paper read before the Royal Society, Edinburgh, April 6th, 1846, and kindly communicated by the Author.

must now lie against the present method of determining the quantity of fluorine present in bodies, consisting as it does in converting that element into fluoride of calcium, which, in the course of the necessary analytical operations, is washed freely, and must be seriously diminished in quantity; a fact which has of necessity been hitherto overlooked.

Dr. Wilson stated, that he was not yet able to suggest an unexceptionable quantitative process; but that, at all events, the fluoride of barium, being much less soluble than the fluoride of calcium, might in the meanwhile be substituted for it in the examination of fluorine.

The author then proceeded to state, that, in consequence of the observation he had made as to the solubility of fluoride of calcium in water, he had been led to look for that body in natural waters, and had found it in one of the wells of Edinburgh, viz. in that supplying the brewery of Mr. Campbell, in the Cowgate, behind Minto House. At the same time he stated, that preceding observers had already found it in other waters. He believed however that he was the first to detect it in sea water, where, by using the *bittern* or mother-liquor of the salt-pans in which water from the Frith of Forth is evaporated, he had found it present in most notable quantity. The author referred to the presence of fluorine in sea water, as adding another link to the chain of observed analogy between that body and chlorine, iodine and bromine.

Dr. Wilson further stated, that he had confirmed the observations of Will as to the presence of fluorine in plants; and Berzelius's discovery, that fluorine exists in the secretion from the kidneys; and had, in addition, detected fluorine in milk and blood, in neither of which has it hitherto been suspected to occur. The paper concluded by some observations on the presence of fluorine in fossils, and its relation to animal life.

ANALYTICAL CHEMISTRY.

On a Method of avoiding the Inconveniences resulting from the Presence of Mercury in the Estimation of Silver by the Moist Process.
By A. LEVOL.

FOR more than fifteen years since the moist process was established by M. Gay-Lussac for the estimation of silver, the accuracy of the results yielded by it has apparently failed only under two special circumstances, fortunately very rare, and which its illustrious discoverer has pointed out himself*. They consist in the presence of sulphur or mercury in the silver submitted to examination. With respect to the sulphur, M. Gay-Lussac, in describing the evil, at the same

* Ann. de Chim. et de Phys., lviii. p. 218, and lxiii. p. 334.

time pointed out the remedy, which is perfect. As regards the mercury, its presence is readily detected in the course of the operation itself by distinct characters; but no method had hitherto been pointed out for restoring to the process the superiority which the presence of this metal appears to deprive it of. After several experiments I have succeeded in overcoming the difficulty in the following manner:—

The sample for assay being dissolved, as usual, in 5 cubic centimetres of nitric acid of 1.283 spec. grav., I supersaturate the solution with 25 cubic centimetres of caustic ammonia, then add the normal liquor, and supersaturate the excess of ammonia with 20 cubic centimetres acetic acid, and continue the operation in the usual manner.

By means of this slight modification of M. Gay-Lussac's process, solely for this exceptional case, I have succeeded, either with the presence or absence of copper, in estimating accurately, by the moist process, silver which contained one-tenth of its weight of mercury, a quantity far exceeding that accidentally met with in the ingots of commerce. The liquids become sufficiently clear by simple agitation, and the precipitate is coloured by exposure to light, as in the absence of mercury.

It appeared to me indifferent, as regards the accuracy of the result, whether the saturation of the ammonia is effected before or after the addition of the normal solution; nevertheless, I thought the liquid became much sooner clear in the last condition.

It may not be superfluous to state, that it is very easy to obtain an excellent result of an assay of silver containing mercury made in the ordinary way, and in which the presence of the mercury is rendered manifest by the non-coloration of the precipitate under the influence of light. It suffices, for this purpose, to dissolve the precipitate in concentrated ammonia, and to supersaturate with acetic acid.

I employ the ordinary acetic acid of commerce, and the ammonia diluted with its volume of water, to avoid the too violent reaction. It is not necessary to state that these two reagents should be perfectly free from chlorides.

This paper being essentially practical, I might dispense here with all theoretical interpretations; I may however state that I explain the utility of the ammonia by admitting that it forms with the nitrate of the binoxide of mercury the double salt described by M. Thenard as the subnitrate of the binoxide of mercury and ammonia. Those chemists who have investigated and analysed this salt are not agreed as to its composition, which may in fact be regarded in various manners, according to the theory of ammonia and its congeners adopted; but they agree respecting its principal chemical properties, and attribute to it, among other things, that of resisting several powerful reagents; it is therefore not surprising that such a salt, with such a remarkable stability, is able to overcome the affinity which the chlorine contained in the chloride of sodium has for the mercury; and thus the result of the assay is no longer affected by the presence of this metal, the chlorine combining exclusively with the silver, and the mercurial salt remaining dissolved, as I have

convinced myself. I may also mention, in support of this explanation, that in all my experiments I have entirely confirmed the assertion of those chemists as to the remarkable solubility of the salt in question in ammonia, and especially in ammoniacal salts. With respect to the acetic acid, it appears to me to play some other part in the reaction than saturating the ammonia, retaining in solution the chloride of silver; to a certain point it might be replaced by nitric or sulphuric acid, but then it would be requisite that these acids should be very dilute in order to avoid the inconveniences accompanying the precipitation of the mercury; but in such cases the liquid would be so dilute as to render the process very embarrassing.—*Ann. de Chim. et de Phys.*, April 1846.

On the Separation of Boracic Acid from Phosphoric and Fluoric Acids. By Prof. VON KOBELL.

I have continued my experiments on the separation of phosphoric acid*, and have precipitated borates and fluorides with an addition of perchloride of iron by means of carbonate of lime, to ascertain whether the phosphoric acid could be separated in this manner from the above acids, and how these would behave.

Some perchloride of iron was added to a solution of borax, and the mixture precipitated with carbonate of lime. As soon as the precipitate was well-washed, it was treated with sulphuric acid and alcohol; but it did not exhibit the least trace of boracic acid, the whole of which had remained in solution. In like manner, a solution of fluor spar in muriatic acid was mixed with perchloride of iron and thrown down with carbonate of lime; the filtered solution was evaporated to dryness, decomposed in a platinum crucible with sulphuric acid, using a glass plate as a cover. Not a trace of fluoric acid was evident. The iron precipitate, treated in the same manner, exhibited the reaction very distinctly; consequently the fluorine is precipitated under these circumstances.

A solution of phosphate of soda and borax was now treated with perchloride of iron, and thrown down with carbonate of lime; in this case likewise the precipitate contained not a trace of boracic acid. A solution of fluor spar in muriatic acid, mixed with borax and perchloride of iron, and precipitated with carbonate of lime, likewise showed that the boracic acid had remained in solution, but that the fluoric acid had been entirely precipitated.

Since carbonate of baryta may be employed instead of carbonate of lime, this method can be used in many cases for the separation of these acids.

With respect to the addition of perchloride of iron, I have found with the phosphates that when the precipitate is of a white colour all the phosphoric acid has not been precipitated, consequently that too little perchloride of iron has been added. In this case more

* See p. 158 of our last number.—*Ed. Chem. Gaz.*

perchloride of iron and carbonate of lime must be added, until the colour of the precipitate becomes red, so that the phosphoric acid is entirely precipitated.—*Journ. für Prakt. Chem.*, xxvi. p. 305.

PATENT.

Patent granted to J. B. Gregson, Dunston, Durham, for Improvements in the Manufacture of Epsom Salts and Carbonate of Lime, commonly called Precipitated Chalk, parts of which Improvements are applicable to other purposes.

THESE improvements in the manufacture of Epsom salts are two in number, and consist,—1st, in the application of sulphuric acid to dolomite or magnesian limestone in the uncalcined state; and 2nd, in the application of muriate of ammonia to remove the lime from the mixed hydrates of lime and magnesia, obtained by thoroughly calcining and slaking dolomite.

The following is the mode of carrying out the first improvement:—The dolomite is reduced to powder, and made into a paste with water, in an open vessel lined with lead; then sulphuric acid, of 1.500 spec. grav., is added in the proportion of 350 lbs. of the latter to 200 lbs. of the former, and the mixture is well-stirred. The sulphuric acid rapidly decomposes the dolomite, and carbonic acid gas is liberated; and when the effervescence ceases, a solid substance remains, composed of the sulphates of lime and magnesia; if desired, the carbonic acid gas may be collected for use, by mixing the sulphuric acid and dolomite in a close vessel. The mixed sulphates are separated by diffusing the solid residuum in water, allowing the sulphate of lime to subside, and drawing off the supernatant liquid, which is a solution of sulphate of magnesia (Epsom salts), containing a small quantity of sulphate of iron; this solution is freed from sulphate of iron by means of caustic lime or magnesia, and is evaporated and crystallized in the usual way. Or the mixed sulphates may be calcined in a reverberatory furnace for 3 or 4 hours, or until the whole of the iron is peroxidized; and, when this has been done, the sulphate of magnesia may be dissolved out of the mass, and the clear solution evaporated and crystallized.

The method of operating according to the second improvement is as follows:—200 lbs. of muriate of ammonia are dissolved in 100 gallons of water, in an iron boiler, by the application of heat, and the solution is allowed to cool; after which 200 lbs. of thoroughly calcined dolomite are slaked with water, and put into an iron still (holding from 300 to 400 gallons), connected with a Woulf's apparatus containing water; the solution of muriate of ammonia is then introduced, and a gentle heat applied to expel the ammonia, which is condensed in the Woulf's apparatus, and stored for use. When all the ammonia has come over, the residuum is withdrawn from the still, and the hydrate of magnesia thoroughly washed, to free it

from muriate of lime. The magnesia is then saturated with sulphuric acid, the iron it contains is thrown down by means of caustic lime or magnesia, and the clear solution is evaporated and crystallized.

The improvements in the manufacture of carbonate of lime consist,—1st, in the application of carbonic acid gas to a solution of caustic ammonia and muriate of lime, and in the recovery of the muriate of ammonia for subsequent use; and 2nd, in adding a solution of carbonate of ammonia (obtained by saturating a solution of caustic ammonia with carbonic acid gas) to a solution of muriate of lime.

With regard to the first improvement, the operation is conducted in the following manner:—100 lbs. of muriate of ammonia are dissolved in 100 gallons of water, and the solution allowed to cool; 70 lbs. of well-burnt lime are then slaked in water, and when cold stirred into the solution of muriate of ammonia in an earthenware vessel; mutual decomposition immediately takes place, and muriate of lime and caustic ammonia are formed in the liquid. This solution is transferred to a cylindrical vessel, lined with lead, and containing an agitator covered with lead; carbonic acid gas is then forced into the solution by means of a force-pump connected with the bottom of the vessel, and the agitator is kept revolving until the solution is entirely decomposed, which may be known by the smell of ammonia no longer arising. The vessel will now contain a milky fluid, composed of carbonate of lime and a solution of muriate of ammonia; this fluid is removed, and allowed to settle; the clear solution of muriate of ammonia is then decanted off, and the precipitated chalk well-washed and dried. The solution of muriate of ammonia may be again used.

The mode of carrying into effect the second improvement in the manufacture of carbonate of lime is as follows:—100 gallons of a solution of caustic ammonia, of 0.970 spec. grav., are introduced into a vessel similar to that last described, and capable of holding 120 gallons; carbonic acid gas is then forced in, and the solution becomes thereby converted into a solution of bicarbonate of ammonia, which is run into a cistern containing 100 gallons of a solution of caustic ammonia, of the same specific gravity; and a solution of carbonate of ammonia, of 1.050 spec. grav., is thus produced. This is mixed with a solution of muriate of lime, of 1.200 spec. grav., in the proportion of 2 parts of the former to 1 of the latter; decomposition immediately takes place, and the whole becomes a gelatinous mass, which must be stirred until the carbonate of lime assumes the solid form. The mass is then allowed to subside, the clear solution of muriate of ammonia is drawn off, and the carbonate of lime is washed and dried.—Sealed Feb. 10, 1845.

THE CHEMICAL GAZETTE.

No. LXXXVI.—May 15, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Presence of Sulphocyanogen in Human Saliva.

By MAX. PETTENKOFER.

As authors are not agreed upon the occurrence of sulphocyanogen in the saliva, Gmelin, Ure, Liebig and Wright, speaking in favour of it, whilst Berzelius, Kühn and Müller are opposed to it, it appeared requisite to the author again to investigate the subject. The saliva used was collected from the author himself, and its secretion was promoted by smoking tobacco. It was acidified with sulphuric acid, and subjected to distillation to separate the volatile acids. After 24 grms. of the fluid had been distilled to about two-thirds, the author observed that when carbonate of lead was put into the receiver, it was blackened by sulphuretted hydrogen. This was supposed to arise from the presence of a metallic sulphuret in the saliva; but none could be detected; moreover, it was shown by another experiment, that sulphocyanide of potassium gave off sulphuretted hydrogen when distilled with sulphuric acid. The carbonate of lead used in the above distillation was boiled with water, and the filtrate evaporated to dryness. The residue was now boiled with alcohol, and the alcoholic extract also evaporated to dryness. On adding sulphuric acid to it, the odour of acetic acid was distinctly evolved. The portion of the aqueous extract insoluble in alcohol was composed of chloride of lead; hence muriatic and acetic acids had passed over. To separate the constituents of the portion insoluble in water, it was treated with a weak solution of carbonate of soda, the filtrate evaporated and exhausted with spirit. The spirituous solution was reddened by chloride of iron. The reddening certainly was less intense than that of the ordinary spirituous extract of saliva; still even this experiment goes far towards proving the presence of sulphocyanogen. The author next determined to examine carefully the means for detecting sulphocyanic acid. It is well known that acetic, formic and meconic acids produce the same reactions with chloride of iron as sulphocyanic acid. It is also known that a solution of peracetate of iron becomes turbid when boiled, but becomes nearly clear again on cooling. The latter phenomenon also occurs when sulphate of potash, nitre, chloride of sodium, &c. are heated with a solution of acetate of iron, and, as the author has observed,

by continued ebullition with a sufficient quantity of chloride of sodium or potassium, the whole of the iron is precipitated; so that on cooling it requires a very considerable quantity of acetic acid to redissolve it. If the reddish-brown precipitate be collected on a filter, at first a transparent fluid passes through, containing no trace of iron; but after continued edulcoration, the precipitate on the filter begins to dissolve. Peroxide of iron and chlorine are detected in the solution; and if a little nitric acid be added to it, the greater part of the iron subsides in bright brown flakes. It has a powerful astringent, but not the least inky taste; and if metallic chlorides be added to it, the peroxide of iron it contains is again precipitated. The above dark brown solution is undoubtedly the basic chloride of iron mentioned by Phillips.

To examine this compound more minutely, the author burnt piano-forte wire in a current of chlorine, and digested the aqueous solution of the chloride thus obtained with hydrated peroxide of iron until the acid reaction and inky taste had disappeared. On estimating the chlorine by silver and precipitating the iron by ammonia, the author obtained the formula $2\text{Fe}\text{Cl}_3 + 2\text{Fe}^2\text{O}_3$. The solution became turbid on evaporation, and hydrated peroxide of iron separated.

Thus, the property of fluids which are of a red colour from the presence of acetate of iron, of being perfectly decolorized on ebullition with alkaline metallic chlorides, enables us to distinguish them readily from the precipitation produced by sulphocyanic acid. Formic acid reacts upon peroxide of iron exactly as acetic acid, except that the precipitation of the iron on boiling occurs much sooner, especially when chlorides are added. The red colour caused by meconate of iron cannot be removed by this means. To distinguish the sulphocyanate of iron from the meconate and the acetate, the author recommends the red ferrocyanide of potassium*. Thus, if the red ferrocyanide of potassium be added to the red solution of chloride of iron and sulphocyanide of potassium, prussian blue falls in a short time, and immediately if heat be applied. The odour of prussic acid also becomes evident. An explanation of this process cannot at present be given with certainty; it may however be remarked, that no products of the decomposition of sulphocyanogen can be detected, but that the greenish fluid again yields prussian blue on the addition of chloride of iron and red ferrocyanide of potassium. The latter salt does not exert the least action upon the meconate, acetate, &c. of iron.

To apply these results to test the saliva, the author evaporated fresh saliva almost to dryness, exhausted it with strong spirit, again

* The red colour produced by the action of sulphocyanic acid upon iron is much more readily distinguished from that produced by meconic, acetic and formic acids, by the action of bichloride of mercury, which destroys the colour of the former but not of the latter, than by the reagents given in the text. We believe this test was proposed by Messrs. Garrod and Marshall. The red colour produced in the saliva on the addition of the chloride of iron is destroyed by the bichloride of mercury.—*Ed. Chem. Gaz.*

evaporated, and dissolved the alcoholic residue in water. The solution was very strongly reddened by neutral chloride of iron, and let fall some brown flakes; but it could not be caused to disappear by the addition of chloride of sodium nor of ammonium. A very minute portion only of the colour could therefore have been caused by acetates. Another portion of the salivary extract was reddened by a few drops of chloride of iron, and treated with red ferrocyanide of potassium, whereupon the formation of prussian blue described above occurred. Another portion of the extract was boiled with chlorate of potash, muriatic acid being at the same time added in drops, chloride of barium then gave a precipitate of sulphate of baryta, which was not the case previously. When the extract was treated with a solution of lead in caustic potash, no formation of sulphuret of lead could be detected; but when it was boiled with sulphuric acid, and a moist piece of lead-paper held over it, it was distinctly rendered brown. By numerous repetitions of the above experiments on the saliva of different persons, the author obtained the same results; so that the occurrence of a metallic sulphocyanide in saliva may be admitted with certainty.

To estimate the sulphocyanogen in saliva, Wright advises us to form sulphocyanide of lead, to weigh this, and to calculate the quantity of sulphocyanide of potassium in the saliva from it. But the metallic chlorides, &c. in the saliva inevitably produce error, consequently, according to Wright's experiments, the amount of sulphocyanogen in the saliva is much too great. Hence the author recommends the oxidation of the sulphocyanogen, so as to form sulphuric acid, and the estimation of the latter by baryta. A weighed quantity of saliva is evaporated, exhausted with alcohol, the latter evaporated, the residue dissolved in water and boiled, chlorate of potash and a little muriatic acid being added. Before adding the muriatic acid, the fluid must be heated to boiling, otherwise a little sulphocyanic acid will escape undecomposed. The author thinks that the small quantity obtained by Kühn may be explained in this manner. 100 parts of sulphate of baryta correspond to 25.11 sulphocyanogen, or 41.91 sulphocyanide of potassium. In this analysis care must be taken that no other sulphur-compound exists in the solution. The alcoholic solution of the solid residue of saliva leaves almost all the sulphates which may be present undissolved. If not, their separation must be previously effected by a soluble salt of baryta; sulphurous acid and hyposulphuric acids must be previously converted into sulphuric acid by peroxide of lead. Metallic sulphurets might be removed by digestion with carbonate of lead. The author ascertained, by counter experiments, that the sulphur of the sulphocyanogen is completely oxidized in the above manner.

The mode of formation of the sulphocyanogen in saliva has hitherto proved a stumbling-block; but if we regard urea as a cyanate of ammonia, $C^2NO + NH^3O$, and compare the formula of sulphocyanide of ammonium with it, $C^2NS^2 + NH^3$, we find a striking relation between them; for if we replace 2 equiv. of oxygen in the urea by 2 equiv. of sulphur, we have the elements of sulphocyanide

of ammonium, $C^2 N^2 H^4 S^2 = C^2 NS^2 + NH^4$. Moreover, the products of decomposition of the two substances on destructive distillation are to a certain extent similar. The author has also found that urea may be converted into a compound of sulphocyanogen by the action of alkaline sulphurets. Since urea occurs already formed in the blood, it would not appear improbable that by combining in the salivary glands with the sulphur of the proteine compounds, it forms sulphocyanogen. Wright has remarked the excretion of urea in the saliva during salivation. It would be interesting to observe whether the saliva contains urea in mercurial ptyalism where the chloride of iron frequently does not cause any reddening.—*Buch. Rep.* xli. p. 289.

On the Citrate of the Oxide of Methyle. By ST. EVRE.

To prepare this æther, the existence of which had been rendered probable by that of the citrate of æthyle, the author dissolved citric acid in hot pyroxylic spirit, and passed a current of dry muriatic gas through the liquid. It was then warmed, to remove the excess of pyroxylic spirit and the hydrochlorate of the methyle, when a yellowish fluid passed over at 194° , which on exposure to the cold deposited after a time tolerably large prismatic crystals, frequently in stellate groups. Pressed between blotting-paper and dried *in vacuo*, they yielded the following results:—

Carbon.....	45.83	46.03	36 = 108	46.15
Hydrogen	5.72	6.02	14 14	5.98
Oxygen	48.45	47.95	14 112	47.87

The formula of this body is consequently $\bar{C}i, 3\bar{M}eO$, or $C^{24}H^5O^{11}$, $3C^4H^3O$. The mother-ley from which the crystals are separated gave different results, which were interesting in so far as they appeared to correspond to a tribasic æther, in which the third equiv. base is replaced by 1 equiv. water, $\bar{C}i, 2\bar{M}eO, HO$:—

Carbon	43.12	42.00	32 = 96	43.63
Hydrogen	6.13	6.23	12 12	5.45
Oxygen	50.75	51.77	12 112	50.92

Comptes Rendus, xxi. p. 1441.

Chemical Investigation of the Red Poppy (Flor. Papav. Rhœad.). By LEO MEIER.

The author found in the poppies, vegetable albumen, gum, starch, rhœadic acid, papaverate of lime, cerine, a soft resin, a fatty oil, wax and woody fibre; and in the ash, chloride of calcium, chloride of potassium, sulphate of potash, sulphate of lime, phosphate of magnesia, phosphate of lime, carbonate of lime and magnesia. Betz and Ludwig mention the occurrence of malic and gallic acid, but this the author is inclined to doubt. The colouring principle of the

flowers consists, according to the author, of two acids, one of which he calls *rhœadic acid*, the other *papaveric acid*.

To obtain the rhœadic acid pure and unaltered, a solution of acetate of lead is poured into a hot concentrated aqueous extract of the flowers; the precipitate which forms is carefully washed, alcohol of 0·889 sp. gr. added to it, and as much sulphuric acid as to leave a portion of the precipitate undecomposed, and the whole heated to boiling. The filtered solution leaves on evaporation a brilliant red amorphous mass, which is dissolved in water, and again precipitated with a solution of acetate of lead. The precipitate is washed with hot water, in which the papavate of lead dissolves, and the residue is then again decomposed with sulphuric acid. This operation is repeated until the liquid above the lead precipitate no longer exhibits any colour. This is more quickly effected by boiling the aqueous extract of the poppies with carbonate of lead, and decomposing the rhœadate of lead with sulphuric acid. On attempting to separate the acid from the lead by sulphuretted hydrogen, it is altered.

Pure rhœadic acid is a shining dark red amorphous mass, void of odour, and of a pure acid taste; on exposure to the air, it slowly absorbs moisture without deliquescing. It has a strong acid reaction, is insoluble in æther, soluble in cold absolute alcohol and cold water. A grain of the acid imparts a red colour to an ounce of water. If the acid is not free from papaveric acid, a reddish-brown residue is each time left on evaporation and re-solution. The acid yields, with a solution of sugar of lead, a bluish-gray precipitate; the same with acetate of copper; a dark turbidness with perchloride of iron; a dark colour with caustic and carbonated alkalies, and a yellow colour with dilute nitric acid. Nitrate of silver, tincture of galls, solution of gelatine, dilute sulphuric and muriatic acid, produce no effect. The salts of rhœadic acid are of a brownish, bluish-gray or violet colour, have no smell, and are most of them tasteless, amorphous, and all of them insoluble in absolute alcohol. The acid is not altered by exposure to the air and light, nor by hydrogen gas, although in the decomposition of the lead salt it acquires a brick-red colour. On treating the solution with chlorine, it becomes yellow, and leaves on evaporation a slight residue. When rhœadic acid is boiled with dilute nitric acid, it assumes a yellow colour, without any evolution of gas taking place. After a time some minute crystals are deposited, and there remains, on removing the nitric acid, a yellowish-brown residue, which yields a brown precipitate with a solution of acetate of lead. Concentrated sulphuric acid, and also excess of caustic potash, convert the acid into a blackish-brown mass, which dissolves in a solution of potash. When rhœadic acid is heated over a spirit-lamp on platinum-foil, it puffs up, and is carbonized without inflaming; on dry distillation, it yields an acid liquid and an empyreumatic oil.

Papaveric Acid.—To obtain this acid as pure as possible, the extract of flowers of poppy, prepared with hot water, is digested with carbonate of lead. The liquid filtered from the rhœadate of lead is

violet, has neither taste nor smell, is neutral towards vegetable colours, and contains no oxide of lead. Oxalic acid produces no precipitate in it, although lime is detected in it on reducing it to ash. Some sulphuric acid is added to the concentrated liquid, when some gypsum separates; it is evaporated to dryness, and the residue treated with alcohol of 60 per cent. The rose-coloured alcoholic extract leaves the acid on evaporation as a shining amorphous mass, of a beautiful red colour. It is deliquescent, has no smell, a slightly acid taste, is not soluble in æther and absolute alcohol, but readily so in spirit and water. Its solution is not rendered turbid by acetate of lead, neutral acetate of copper, nitrate of silver and perchloride of iron; alkalies, barytic and lime-water, and protochloride of tin, colour it violet; dilute acids do not alter it. Its salts are brown, amorphous, have neither taste nor smell, are soluble in water, and most of them soluble in spirit of 0.912 sp. gr. The acid can be separated from all of them, if they had been rapidly evaporated *in vacuo*, by dilute sulphuric acid; but if slowly at a gentle heat, the salts assume a black colour, leave on solution a black residue, and yield on the addition of sulphuric acid the papaveric acid with a yellowish-brown colour. If a few drops of dilute sulphuric acid are added to a solution of papaveric acid, a dark sediment subsides, which is also formed by the action of acetic acid.—Buch. *Rep.*, xli. p. 235.

Chemical Examination of the Inner Bark of the Elder Tree
(*Sambucus nigra*). By H. KRAMER.

The central green bark of the elder has an odour similar to the leaves of this tree, and a disagreeable bitter taste. The brown decoction is rendered darker by ammonia, yields a black-precipitate with protoperchloride of iron, a white precipitate with acetate of lead and a solution of corrosive sublimate, and a dirty white precipitate with nitrate of silver. Tartar-emetic only produced a turbidness after some time; chloride of barium and oxalic acid gave slight white precipitates. The water distilled over the fresh bark somewhat resembled in smell the *Aq. Cort. Viburn.*, and faintly reddened litmus-paper. By digestion with carbonate of baryta and evaporation, a salt was obtained which possessed all the properties of viburnate of baryta already described by the author*. The water which escapes on evaporating the saline solution, still contained slight traces of an essential oil. Triturated with water and pressed, the bark yielded a clear liquid, which on boiling deposited flakes of albumen.

The æthereal extract of the bark, dried in the water-bath, possessed a beautiful green colour, and yielded on evaporation a green smeary mass, from which water extracted a small quantity of a tan-

* Viburnic acid likewise occurs, according to the author, in the *Floris Sambuci*. It is combined in the *Aqua Sambuci* with ammonia, and occurs with essential oil and carbonate of ammonia. [This viburnic acid has been proved by Monro to be nothing more than valerianic acid. See p. 9 of the present volume.—Ed. *Chem. Gaz.*]

nin yielding a black precipitate with iron. Cold alcohol dissolved the mass with the exception of a green soft substance; an alcoholic solution of acetate of lead was mixed with this solution, the bright green precipitate collected on a filter, and the filtered liquid freed from excess of lead by sulphuretted hydrogen. On evaporation, it left a light brown transparent resin, which dissolved readily in æther, sulphuret of carbon, oil of turpentine and oil of almonds; less readily in alcohol, from a boiling saturated solution of which it is again partially deposited on cooling in the form of a powder. The solution has a bitter irritating taste; it does not redden litmus. It does not dissolve in acetic acid, nor in solution of ammonia or potash, and consequently belongs to the perfectly neutral resins. The lead precipitate was treated with alcohol and sulphuretted hydrogen. The filtered solution yielded on evaporation a dark brown smeary mass, of a disagreeable odour, which melted when warmed and stained paper. It dissolved readily in æther, sulphuret of carbon, fat and essential oils, and with tolerable ease in alcohol, which solution reddens litmus. On saponifying this fat, and then decomposing it with sulphuric acid, it diffused the disagreeable odour more distinctly. On combustion with nitre, it left a saline mass, which gave a precipitate with chloride of barium after saturation with muriatic acid, and consequently contained sulphur, which could not have arisen from the treatment with sulphuretted hydrogen. The portion of the æthereal extract which would not dissolve in cold alcohol contained wax and chlorophylle.

The alcoholic extract of the bark was of a light brown colour, had an acid reaction, and left a brown transparent hygroscopic extract, soluble for the greater part in water. The tannic acid contained in it was precipitated by a solution of acetate of lead, the excess of lead removed by sulphuretted hydrogen, the liquid filtered and evaporated. In this extract grape-sugar was detected by the potash and copper test, and in the ash carbonate of potash. To determine the acid combined with the potash, the lead precipitate was boiled with water and filtered hot, when on cooling crystals of malate of lead separated. The portion of the alcoholic extract insoluble in water contained the above-described mixture of resin and fat.

The cold infusion of the bark was of a light brown colour, tasteless, and yielded on evaporation a transparent light brown mass, which on treatment with boiling alcohol became nearly colourless. It dissolved in a little water to a colourless liquid, which exhibited the reactions of Liebig's mucilaginous gum. It left on combustion a small quantity of carbonate of lime, which was probably contained in the plant as malate of lime. The extract remaining after evaporation of the alcoholic solution had a bitter taste, and gave precipitates with acetate of lead, nitrate of mercury and silver.

The extract obtained with dilute muriatic acid was reddish-brown: it was evaporated in the water-bath to the consistence of thin honey, and alcohol added to it, which precipitated brown mucilaginous flakes. These, after being well-washed with alcohol, were tasteless, and behaved precisely like the artificial gum which is formed on

treating amylaceous plants with muriatic acid. Evaporated to dryness and extracted with water, the alcoholic solution, which contained some tannic acid, deposited a sediment of extractive. The ash of the muriatic extract consisted of chloride of calcium, sulphate and phosphate of lime, magnesia and chloride of potassium.

The alkaline decoction of the bark was evaporated in the water-bath, and then treated with acetic acid, which produced a flocculent brown precipitate, from which boiling acetic acid removed coagulated vegetable albumen, leaving a residue of pectine.

According to the experiments of the author, the central bark of *Sambucus nigra* contains viburnic acid, traces of an essential oil, vegetable albumen, a neutral resin, an acid sulphurous fat, wax, chlorophylle, tannic acid, grape-sugar, gum, extractive, starch, pectine, malate of potash, malate of lime, sulphate of potash and lime, chloride of potassium, phosphate of magnesia, lime, silica, and peroxide of iron.—*Archiv der Pharm.*, xliii. p. 20.

On the Digestion and Assimilation of Amylaceous and Saccharine Substances. By M. MIALHE.

The essential basis of the nutrition of animals consists of three groups of very distinct bodies; these are albuminous, fatty and saccharine matters. But these substances are not all immediately assimilable; to become so, it is requisite that they should remain a longer or shorter time in the gastric and intestinal cavity, and should there undergo a kind of liquefaction or fermentation—a chemico-physiological process which is called digestion.

The chemico-physiological study of the groups of alimentary substances is far from equally advanced, although so many excellent chemists have investigated the subject. It is generally admitted,—1st, that albuminous substances are only assimilable through the action of the gastric juice, which by means of its acid being loaded with nitrogenous matters, and by its pepsine which is a true ferment, causes their solution—an analogous phenomenon to the action of diastase upon starch; 2nd, fatty matters are rendered assimilable by the action of the bile. But nothing positive is known regarding the amylaceous and saccharine matters, except a few scattered facts and hypotheses void of foundation. I have investigated this point, and by discovering the active principle of the saliva, a substance which appears identical with diastase, and which can be isolated in the same manner as it, I can give the true explanation of the phenomena of the transformation of the cellular amylaceous substances into saccharine matters.

The active principle of the saliva is solid, white or whitish-gray, amorphous, insoluble in alcohol, but soluble in water and dilute alcohol. Its aqueous solution is neutral, and is not precipitated by the diacetate of lead; when set aside, it soon becomes changed and acid. The acid which is produced is either butyric acid or one very similar to it. This principle has no action upon the nitrogenous substances, fibrine, albumen, caseine, gelatine and gluten; nor upon the neutral

ternary matters, cane-sugar, inuline, gum-arabic and woody fibre; but its action upon starch is very extraordinary. When a mixture of this principle is heated in the sand-bath to 158° or 176° F., with a mixture of starch and water (1-8), each grain of starch, as it becomes hydrated, is instantly rendered soluble. After a time the solution is not coloured by iodine, and on heating it with potash it yields an intense brown colour; sure indications that the starch is converted into dextrine and glucose*, a fact which is equally confirmed by filtering the liquid, and treating it with 6 or 8 times its weight of absolute alcohol. The latter retains the glucose in solution, and precipitates the dextrine.

This principle, like diastase, contains nitrogen. I shall denominate it animal or salivary diastase. It is prepared by filtering the saliva, and treating it with 5 or 6 times its weight of absolute alcohol; being insoluble in this reagent, it is precipitated in white flakes. These are collected on a filter, and placed whilst moist in thin layers upon a plate of glass, dried in a current of air heated to 104° - 122° F., and preserved in a well-closed bottle. Its proportion in human saliva rarely exceeds $\frac{2}{1000}$ ths.

Admitting that the influence of the alkalies enables the solutions of glucose to reduce the binoxide of copper, and hence considering that the assimilation of amylaceous and saccharine substances only ensues when alkalies are present, I believe that diabetes arises rather from a defect in the assimilation of sugar than in an increased production of this principle.

The main points in the author's paper have been confirmed by a commission of the French Academy.—*Comptes Rendus*, March 31, 1845, and April, 1846.

Chemical Investigation of some Papaveraceæ. By Dr. RIEGEL.

With a view of submitting the several members of the family of the *Papaveraceæ* to an accurate analysis, similar to those which have been published by Probst, Walz and others, on *Chelidonium*, *Clausium*, *Eschscholtzia*, &c., the author began with *Radix Sanguinaria*. The dried and powdered root was exhausted with æther, and muriatic acid gas passed through the solution, when a beautiful red precipitate of muriate of sanguinarine subsided. To obtain from this the sanguinarine prepared by Dana, it was dried, dissolved in water, and thrown down with an excess of ammonia. The pearl-gray precipitate which formed was washed, dried, dissolved in æther, decolorized with animal charcoal, and then again treated with muriatic acid, &c. Sanguinarine is a yellowish tasteless powder, which causes violent sneezing, and is immediately coloured red by contact with acids. The alcoholic solution has a decided alkaline reaction. When heated, it melts to an oil and burns. With acids it yields red salts, which are readily soluble in water and are very bitter. Chlo-

* It also reduces the binoxide of copper in salts, and the hydrate when potash is present.

ride of platinum gives with it an orange-red, infusion of galls a yellowish-red precipitate; nitric acid decomposes it. Its formula, according to Scheele, is $C^{97}H^{16}NO^8$.

A second alkaloid occurs in the root of *Sanguinaria*, which is obtained by extraction with water containing acetic acid, precipitation of the sanguinarine by ammonia, neutralization of the wash-water with acetic acid, and precipitation with infusion of galls; the deposit is collected, well-washed, dried, and digested with an alcoholic solution of potash as long as anything is dissolved, carbonic acid passed into the solution, and the spirit removed by distillation. The residue is exhausted with water, this evaporated, and what remains extracted with æther, from which it separates on evaporation as a dirty-white crystalline mass. By solution in alcohol and treatment with animal charcoal, it is obtained in small colourless tabular crystals, which are void of taste and smell, and are very sparingly soluble in water, more readily so in alcohol. It yields with acids colourless crystalline salts, which have a bitter taste, dissolve in water, and from whose solutions it is precipitated of a white colour. From want of material no further experiments could be made with it; however, its resemblance to the porphyroxine discovered by Merck in opium, induced the author to prepare the latter in larger quantity. For this purpose, powdered Smyrna opium was exhausted with boiling æther; the residue, after distilling off the æther, was repeatedly boiled with water, the solution evaporated, the residue dissolved in æther, decolorized with animal charcoal, evaporated, and the meconine obtained recrystallized from water. The æthereal extract, which had been exhausted with water, was treated with boiling alcohol as long as this removed anything. The crystalline mass, which separated on cooling and evaporation, was dried, dissolved in boiling alcohol, and an excess of caustic ammonia added to it; the precipitate formed was dissolved in muriatic acid, and the solution evaporated to the consistence of a syrup, when some crystals gradually separated, which were removed from the liquid, dissolved in boiling water, decolorized with animal charcoal, and precipitated with caustic ammonia. This precipitate was dissolved in boiling alcohol of 0.863 spec. grav., and the solution evaporated, when on cooling colourless crystals of narcotine separated. The liquid separated from the muriate of narcotine was precipitated with an excess of ammonia, and the deposit dissolved in boiling alcohol, when, on evaporation, minute shining needles of porphyroxine separated. The residue of the æthereal extract, after exhaustion with water and spirit, was now treated with a solution of caustic potash, and in this way the fat and resin separated from the caoutchouc.

The portion of the opium insoluble in æther was repeatedly exhausted with water, and the extract boiled with some chloride of calcium; on cooling, a mixture of meconate of lime separates along with muriate of morphine and codeine, which latter is separated from the first by extraction with water. The morphine was precipitated after the meconate of lime had been entirely removed with ammonia, the residue crystallized, solution of caustic potash added

to it, the separated mass washed with water, dried, and treated with æther, from which, after repeated solution and evaporation, pure codeine crystallized. The black syrupy mass, which separated with the meconate of lime, muriate of morphine and codeine, is treated with water containing muriatic acid, and precipitated with ammonia. Thebaine may likewise be extracted by æther from the morphine precipitate. The liquid which has been precipitated with ammonia deposits on evaporation narceine, which is purified by recrystallization.

Porphyroxine crystallizes in colourless, minute, shining needles, is neutral, is coloured of an olive-green by concentrated nitric or sulphuric acid, and is dissolved by dilute acid, becoming red on boiling. Alkalies destroy the colour. The acid solution yields a dirty red precipitate with solution of gold, a rose-coloured one with acetate of lead, and a brown precipitate with protochloride of iron. When heated, it melts, becomes resinous and friable. The author suspects that the porphyroxine is identical with sanguinarine, as well as with cholerythrine, and the alkaloid discovered by Walz in *Eschscholtzia Californica*.—*Jahrb. für Prakt. Pharm.*, xi. p. 100.

On a new Acid in the Root of Robinia. By HUGO VON REINSCH.

The author was induced, by the liquorice-like smell and taste of the acacia-root, to submit it to chemical examination; in the course of which he discovered a peculiar acid, *robinic acid*, which occurs in the root in combination with ammonia. The presence of this salt is readily detected, even by exhausting with boiling water only 2 drms. of the root, evaporating the filtered solution to the consistence of a syrup, and setting it aside for some time. In the course of 12 hours, a tolerable quantity of hard rhombohedrons of robiniate of ammonia, with a vitreous lustre, will be found to have separated. This salt dissolves without colour in 20–30 parts water, is void of taste and smell, and has no action on litmus-paper. The hot concentrated solution is not altered by carbonate of soda; with chloride of calcium it yields a flocculent crystalline, and with chloride of barium a pulverulent precipitate; peracetate of iron produces a yellowish turbidness, nitrate of silver a slight opacity, protosulphate of iron a white precipitate, basic acetate of lead a white precipitate after some time, and protonitrate of mercury a flocculent white precipitate. As the acid forms with lead a soluble compound, the author combined it with protoxide of mercury, and treated this with sulphuretted hydrogen. In this way a colourless syrup was obtained, which on the addition of alcohol became converted into a mass of acicular crystals. From the smallness of the quantity, it could not be submitted to more accurate investigation. Besides the robiniate of ammonia, there also occurs in the root, sugar (no glycyrrhizine), fat and essential oil, chlorophylle, wax, tannic acid, a yellow colouring principle, which becomes reddish brown by alkalies, mucilage, much albumen, starch, salts, and an alkaloid, which the author has not yet succeeded in isolating.—*Jahrb. für Prakt. Pharm.*, xi. p. 423.

*On the Action of Soluble Protosalts of Iron on Vegetation.**By M. GRIS.*

According to the author, the soluble protosalts of iron, when they are absorbed by the roots or leaves of the plants, give rise to an increased production of chlorophylle, especially in chlorotic specimens. The author thence draws the conclusion, that the action of the iron is identical in the vegetable and in the animal kingdom, and that the formation of chlorophylle is not, as is generally admitted, dependent on the action of light. The soluble protosalts of iron are also stated to further the growth, especially of pot plants.—*Comptes Rendus*, xxi. p. 1386.

CHEMICAL PREPARATIONS.

*On the Preparation of Valerianate of Zinc.**By MM. FREDERKING, HENNY and DUMESNIL.*

FREDERKING distils 12 lbs. of valerian-root with 45 lbs. of water over a good fire. When 25 lbs. have passed over, hot water is again added to the residue, and this repeated as long as the distillate reddens litmus. The 50 lbs. of liquid which pass over are heated nearly to boiling, and then a previously weighed solution of carbonate of soda (1 part to 3 parts water) added until the liquid presents a slightly alkaline reaction; this required 3 oz. crystallized carbonate of soda. The liquid is now evaporated down to 4 lbs., and then separated by filtration from a resinous residue, which was again exhausted with 3 drms. crystallized carbonate of soda and 12 oz. of boiling water. The filtered solutions are now evaporated to 8 oz., along with 3 oz. of sulphate of soda to raise the boiling-point; and a sufficient quantity of sulphuric acid (9 drms.) added to saturate the carbonate of soda employed in excess, and distilled to dryness, when at first a limpid fluid passes over, and subsequently the hydrated acid. The latter is dissolved in water, and boiled for 2 hours in a retort with recently precipitated carbonate of zinc, filtered, the residueedulcorated, and the filtered solution evaporated in a retort. The liquid which now passed over still saturated 50 grs. hydrate of baryta, from which 4 scruples of valerianate of quinine were obtained with sulphate of quinine. The concentrated solution of the valerianate of zinc, removed from the retort, was further evaporated in a dish, collecting on fine linen the saline pellicle as it appeared, which was then pressed between blotting-paper. The residue, evaporated to dryness, yielded a somewhat coloured salt. With the above quantity of valerian root, 6-7 drms. of zinc salt may be obtained.

Henny draws attention to disadvantages of the above method, as the concentration of the saline solution in a retort, as also the further evaporation, require too much time, and are moreover attended with loss. They are avoided by using, for the preparation of the

zinc salt, valerianate of soda and sulphate of zinc. When, for instance, a hot concentrated solution of the valerianate of soda is mixed with a hot solution of sulphate of zinc, the sparingly soluble valerianate of zinc separates in beautiful white laminæ, of a mother-of-pearl lustre. If the liquid be now allowed to cool perfectly, and the magma of crystals brought on to linen and pressed, a beautiful preparation is obtained; a further quantity of the salt may be procured by concentrating the filtered liquid.

Dumesnil recommends the following process:—A copper still is filled with valerian root and a little water, and distilled until the product has no longer an acid reaction; it is then saturated with carbonate of soda, and evaporated in the retort to spec. grav. of 1.030. The residue of the first distillation may still be used, according to the author, for the preparation of an extract equal to that obtained by decoction. The product, saturated with soda and concentrated, is acidified with some sulphuric acid, and distilled until the contents of the retort begin to thicken. The turbid acid distillate is mixed with recently precipitated carbonate of zinc till it ceases to effervesce, when it is filtered and well-washed. The filtered solution is then evaporated, and the pellicle skimmed off as it forms. By pressure between blotting-paper, the salt may be entirely freed from mother-ley.—*Archiv der Pharm.*, xliii. p. 2, and xlv. p. 173.

On the Preparation of pure Phosphoric Acid by the Oxidation of Phosphorus with Nitric Acid. By F. L. WINCKLER.

As it is of great importance, according to the experiments of Weigel and Krug, to obtain the phosphoric acid used in medicine free from phosphorous and arsenic acid, the author proposes the following process:—The phosphorus is conveyed as usual in small portions into the heated nitric acid, most advantageously by filling an ovate recipient with a tolerably long neck, half-full with pure nitric acid of 1.300 spec. grav., then heating it in the water-bath, and adding gradually for every 8 parts 1 part of phosphorus, in quantities of about 2 drms. in weight, and with the precaution that it does not inflame in the neck of the recipient. The phosphoric acid thus formed is evaporated, with the addition of one-twentieth nitric acid, until no further nitrous vapours are given off, when the heating is cautiously carried up to 392° . As soon as no more water escapes the phosphoric acid has become entirely converted into pyrophosphoric acid ($\text{PO}^5 + \text{HO}$). The acid is now diluted with 4–6 parts water, and the solution saturated with sulphuretted hydrogen, when it acquires a brownish-yellow colour. Upon this it is boiled until the whole of the sulphuret of arsenic has separated and the sulphuretted hydrogen expelled; it is then filtered and washed, until the liquid amounts to 10 times the weight of the phosphorus employed. The solution contains the ordinary phosphoric acid ($\text{PO}^5 + 3\text{HO}$), and not a trace of phosphorous acid or arsenic; after some time however some milk of sulphur separates, which must be removed by filtration.—*Jahrb. für Prakt. Pharm.*, xii. p. 3.

*On the Preparation of Benzoic Acid.**By Dr. L. BLEY and E. DIESEL.*

The authors found, on comparing the various methods hitherto recommended, that no one perfectly answered the purpose, and propose the following :—8 parts of coarsely-pounded benzoin are heated to boiling with 3–4 parts hydrate of lime and 80 parts water, with constant stirring. The mass, pressed between linen, is boiled again twice with a little water, and again submitted to pressure. When the liquid has become sufficiently clear, it is filtered, and is evaporated down to one-fifth; a slight excess of muriatic acid is then added to it, when the acid separates in beautiful crystals on cooling. It is purified by resolution in hot distilled water, filtration and crystallization. On concentrating the liquid containing the chloride of calcium and the wash-water from the separated acid, a further quantity of slightly-coloured benzoic acid is obtained. 100 parts benzoin from Siam yielded 7 parts of pure and $1\frac{1}{2}$ part of somewhat coloured acid. Another kind gave 11 per cent. pure and 2 per cent. slightly coloured acid. A sample of *Styrax amygdaloides* yielded 13 per cent. pure and 2 per cent. impure acid. According to the experiments of the authors, the proportion of acid seems to vary in the different kinds, but the *Styrax amygdaloides* appears to contain most.—*Archiv der Pharm.*, xliii. p. 17.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

*On the Composition of some Glasses manufactured in Bohemia.**By E. PELIGOT*.*

AMONG the numerous and varied products of industry exhibited at the Exposition held at Vienna 15th May 1845, my attention and study were especially directed to the articles of glass manufacture represented by the productions of the two most famed countries for the manufacture of glass, Bohemia and Venice. In investigating at the localities the various processes connected with this beautiful art, I collected numerous notices, and some specimens of glass, of which I have just completed the analyses. As the composition of these glasses may present some interest, both in a scientific and industrial point of view, I forward them for publication.

It is known that the fine glass of Bohemia differs from our crystal (French), in the latter containing from 30 to 35 per cent. oxide of lead, while Bohemian glass does not contain a trace. The composition of the white glass of Bohemia appears to vary but very little in the numerous manufactories of that country. I have lately analysed (and in 1837, in the laboratory of M. Dumas) various specimens of perfectly pure and colourless glass; they have all yielded very

* It is scarcely necessary that we should direct the attention of the reader to the excellent article on the manufacture of Bohemian glass in our third volume.—*Ed. Chem. Gaz.*

nearly the same results, their composition being represented by the following numbers :—

Silica	76
Potash	15
Lime	8
Alumina	1

Agate Glass.—For some years past the Bohemians have manufactured a kind of semi-opaque glass, presenting the lustre and transparency of agate or of hyaline quartz, without exhibiting the reddish tints of the opaline glass made with phosphate of lime. The composition of this glass, which is also known under the name of *rice-paste*, is remarkable; it is a simple silicate of potash, the semi-opacity of which is owing to an incomplete vitrification, which has left some particles of unfused quartz diffused throughout the mass. According to my analysis, it contains—

Silica	80.9
Potash	17.6
Alumina and traces of oxide of iron	0.8
Lime	0.7

This glass does not absorb moisture from the air; water does not attack it even with prolonged ebullition, as would seem should result from its composition. It differs from the soluble glass, which M. Fuchs proposed to deprive wood and tissues of their inflammability, in containing about 10 per cent. more silica than the latter. Our French manufacturers of crystal likewise produce *agate glass*; but their glass has a very different composition, to judge from the analysis of a sample, which contained a large proportion of lead and lime. The agate glass replaces in Germany our opal glass; being less fusible than the latter, it stands gilding, silvering, and the fire colours better. This advantage exists indeed for all the glasses manufactured in Bohemia, and especially, to the great regret of French chemists, for the glass apparatus used in our laboratories and chemical works. Wood costs in Bohemia one-third or one-fourth less than in France.

Artificial Aventurine.—A sample of this curious product, from the works of Bigaglia at Murano, yielded the following results :—

Silica	67.7
Lime	8.9
Peroxide of iron	3.5
Oxide of tin	2.3
Metallic copper	3.9
Oxide of lead	1.1
Potash	5.5
Soda	7.1

It moreover contains traces of alumina, magnesia, and phosphoric or boracic acid.

The preceding numbers agree tolerably well with those of the analysis of an analogous product, published in 1842, by M. Wöhler*. That chemist however fixes at 6.5 per cent. the proportion of iron,

* This analysis will be found at p. 245 of vol. i. of this Journal.

at 4.5 that of the magnesia, and at 1.5 that of the phosphoric acid; he found only traces of tin, and does not point out the presence of lead.

The artificial aventurine of Venice forms a mass of a slight yellow colour, transparent in thin sheets, and in which the small crystals of copper are diffused. It is probable that the tin and the iron act at first simultaneously, causing the formation of those crystals; it is likewise probable that after they are formed the tin exists in the state of protosilicate, for in the form of stannic acid it would impart to the vitreous mass an opacity which it does not exhibit. The lead occurs in so minute a proportion in the aventurine, that it is probable it was introduced in the state of an alloy of lead and tin.

The composition of the Venetian aventurine differs considerably from that of the glass obtained by Fremy and Clemandot*, on fusing a mixture of 300 parts of powdered glass, 40 parts protoxide of copper and 80 parts iron scale; this glass would contain at least 20 per cent. oxide of iron, and 8 to 9 per cent. copper and oxide of copper; and indeed it presents an opacity and a dark colour, which the Venetian products do not possess.

Blown Mirror Glasses.—The manufacture of cast mirrors, the pride of our industry, does not exist in Germany†. All the mirrors are first blown in the form of a leg of mutton, then expanded in a peculiar furnace arranged nearly like that used to flatten window-glass, and lastly polished by the ordinary processes. The analysis of a specimen from a manufactory of mirrors in Bohemia gave the following numbers:—

Silica	67.7
Lime	9.9
Alumina	1.4
Potash	21.0

This glass is perfectly annealed; its tint is good, although slightly yellowish. The products of this fabrication however are far inferior in respect to dimensions, polish, and frequently in tint, to the cast mirrors of St. Gobin and Cirey; nevertheless this branch is exceedingly interesting in an artistical point of view. At the Exhibition of Vienna there was a blown glass 7 feet in height to $3\frac{1}{2}$ in breadth. It is scarcely possible to conceive how a man can blow a cylinder of such a weight and such dimensions, that so large a plate of glass can be obtained from it, keeping it at the same time of sufficient thickness to be polished.—*Comptes Rendus*, March 23, 1846.

On the Employment of Essence of Turpentine as a Solvent for Caoutchouc. By M. BOUCHARDAT.

About ten years since I was consulted, by a manufacturer of waterproof fabrics, as to the best solvent for caoutchouc. At that time either essential oil obtained by distilling coal-tar, or oil obtained by the open distillation of caoutchouc, was used in England.

* See p. 141 of the present volume.

† The author is mistaken. See vol. iii. p. 305 of this Journal.

I commenced by carefully studying the nature of this pyrogenous oil, and separated from it several kinds of carburetted hydrogen, remarkable by their point of ebullition being very low; I was not long however in being convinced, that if pyrogenous oil of caoutchouc is a good solvent of that substance, its cost will prevent its being for some length of time employed. The essential oil, obtained by distillation from tar, has a disagreeable smell, from which it is so difficult to free the fabrics, that I determined to find, if possible, another solvent.

From the first I thought of a natural carburetted hydrogen (essence of turpentine), which it is well known acts as a solvent of caoutchouc. I hoped that by modifying it by heat, its solvent properties might be augmented; I was confirmed in this idea by experiment. By distilling this essence openly, once or twice, a solvent is obtained which gives satisfactory results. I also remarked, that by effecting this distillation upon fire-brick, the essence being submitted to a higher temperature, a liquid was obtained which was very little inferior as a solvent to the pyrogenous oil of caoutchouc.

The manufacturer who had consulted me hastened to profit by the results which I had obtained; and having reserved the right of publishing them, I made them known in my treatise upon the products of distillation of caoutchouc, inserted in vol. xxiii. of the '*Journal de Pharmacie*.' Since that time, the essence of turpentine, modified by one or two open distillations, has been the solvent for caoutchouc employed by manufacturers of waterproof fabrics in both France and England.

The following are the physical properties possessed by essence of turpentine, obtained by open distillation upon fire-brick. Its colour is yellowish; its smell partakes of that of thyme, oil of naphtha and essence of turpentine; it is lighter than the essence from which it was made in the proportion of 0.8420 to 0.8726. Its boiling-point is 185° F.; but the temperature rises immediately afterwards to 309°, and remains stationary at that point. I endeavoured to isolate the former more volatile portions; but, notwithstanding great care and the best refrigerating mixtures, I was only able to separate a very small portion, insufficient for examination. In general the improved essence has been found to boil at 309° F., whilst before its distillation its boiling-point varied from 313° to 316° F. I analysed the modified oil, and found that its composition was exactly the same as that of the primitive essence.—*Bulletin de Musée de l'Industrie*; as inserted in the *London Journal of Arts*, May 1846.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

April 6, 1846. (The President, Professor Graham, in the Chair.)
The following papers were read:—

"On the Action of Hyponitric Acid upon Aqueous Solutions of Bromine and Chlorine," by Dr. C. F. Schönbein.

Dr. Schönbein finds, that when a solution of bromine or chlorine in water is subjected to the action of hyponitric acid, hydrobromic or hydrochloric acids and nitric acid are formed; and also that if pure nitric acid is introduced into hydrochloric or hydrobromic acid gas, even at a temperature of 15° below zero of Reaumur, these gases are rapidly decomposed, bromine or chlorine with hyponitric acid being eliminated; and that if water be then added, these will disappear, hydrochloric or hydrobromic acid and nitric acid being formed.

"On the Substances contained in the *Roccella tinctoria*," by Mr. E. Schunck.

After briefly adverting to the substances examined and described by Heeren and Kane derived from this lichen, the author proceeds to detail the processes followed by him in the separation of the various substances from the *Roccella tinctoria*, which are the subject matter of the present paper, and then passes to their more perfect description. The first of these is erythric acid, which gives rise to the colouring matters for the production of which this lichen is employed. Mr. Schunck details the properties of this interesting body, and shows that, like lecanoric acid, it is converted by alkalis into oricine and carbonic acid; by long boiling with alcohol, into erythric æther; and by water, under the same circumstances, into picroerythrine. Its composition is $C^{34} H^{19} O^{15}$. The properties, composition and rationale of formation of erythric æther and picroerythrine are next given; and the paper concludes with the roccellic acid, a species of fat acid having the formula $C^{24} H^{43} O^6$, the properties of which are fully detailed.

PATENTS.

Patent granted to Augustus Julien Van Oost, Gaidbrugge, near Ghent, for Improvements in treating Seed, and in preparing Materials used for fertilizing Land, and for aiding Vegetation.

THE object of the first part of this invention is to apply to the corn or other seed a coating of "sulphuro-azoted principles," which, being absorbed by the young plant, or acting as a ferment, will aid vegetation in a considerable degree; and for this purpose the patentee employs a solution of gelatine, albumen, fibrine or caseine, together with certain other matters.

A solution is prepared by dissolving $2\frac{1}{4}$ lbs. of gelatine in 6 gallons of water, and $2\frac{1}{4}$ lbs. of the meal of malt or wheat are mixed therewith; the corn or other seed, which has been first moistened with a solution of ammoniacal salt or carbonate of potash at a density of 10° , is then introduced into the solution. When the seeds have become covered with the preparation of gelatine, they will adhere to each other, and to separate them, a powder (described below) must be used, which, adhering to the gelatinous grains, will form a coating thereto; and thus materials to act as a ferment, and others to moderate this action, will be applied to each grain. The powder

is prepared in the following manner:—50 lbs. of ashes (such as most closely resemble chemically the ashes produced by burning the plant, the seed of which is to be treated), 50 lbs. of carbonate of lime, or lime slaked in the air, 1 lb. of sulphate of iron, 25 lbs. of ground bones, and 25 lbs. of pigeons' dung, are well-mixed; the patentee then dissolves 1 lb. of gelatine, $\frac{1}{2}$ lb. of sulphate of potash, $\frac{1}{2}$ lb. of carbonate of potash, $\frac{1}{2}$ lb. of nitrate of potash, $\frac{1}{2}$ lb. of ammoniacal salt, $\frac{1}{2}$ lb. of phosphate of soda, and $\frac{1}{2}$ lb. of sulphate of soda, in 6 gallons of water or putrid urine; the two mixtures being combined, a moist powder is produced, which is dried at 150° F., and then used for coating the seeds.

Although only gelatine is mentioned in the above description, the other sulphuro-azoted matters may be used in place thereof, or combined therewith; the object being to add a further quantity of sulphuro-azoted principles to that already possessed by the grain or seed, as caseine in peas and beans, fibrine in corn, and albumen in seed.

The patentee does not confine himself to the exact proportions above mentioned, so long as gelatine, albumen, fibrine or caseine, or matters containing them, are applied so as to adhere to the grain or seed, together with matters suitable for modifying the fermentation; and he states that the juice of vegetables, blood, milk, cheese, the flesh of animals, and generally all organic liquids, which have a tendency to corrupt, ferment or putrify, owe this property only to the sulphuro-azoted principles, albumen, fibrine and caseine, which the oxygen of the air converts into ferment as soon as it meets them in a suitable state.

The second part of this invention consists in the preparation of manure to be applied to land: 4 parts of ashes (similar to the ashes of the crop to be grown), 2 parts of pulverized rubbish of buildings, 2 parts of pulverized coal or coke, 2 parts of lime slaked in the air, and 1 part of gelatine, are thoroughly mixed; then 1 lb. of sulphate of iron, 1 lb. of sulphate of potash, 1 lb. of nitrate of potash, 1 lb. of common salt, and $\frac{1}{2}$ lb. of phosphate of soda, are dissolved in 6 gallons of water, and added to 100 lbs. of the aforesaid mixture; after which the whole is dried at 150° F., reduced to powder, and applied to the land. The proportion in which the manure is used varies according to the nature of the soil; the average proportion is 250 lbs. per acre.

The peculiar character of this part of the invention consists in the use of sulphate of iron, of gelatine, and of the sulphuro-azoted matters above mentioned, and in their close mixture with the alkaline salts and inorganic matters, as above described, so as to favour a slow and regular decomposition.—Sealed Oct. 6, 1845.

Patent granted to G. F. Wilson, G. Gwynne, and J. P. Wilson, for Improvements in the Manufacture of Soap.

This invention consists in manufacturing soap from fatty or oily matters, previously hardened with sulphuric acid.

10 tons of palm oil, whale oil, or other fatty or oily matter, are put into a wrought iron vessel, provided with a perforated steam-worm, through which steam is admitted until the matter is heated to 350° F. The fatty matter is then run into a tank, formed of brick, lined with lead, and sunk in the ground; the tank is furnished with a pipe for the introduction of steam, but which does not terminate in a worm, as the sediment from the fat would be likely to choke a worm; the cover of the tank is made of wood, lined with sheet lead, and has two man-holes, closed by an oil joint, about 8 inches deep; through the cover a pipe passes, connected with a high shaft, to allow offensive vapours to escape; or the mixed vapours are allowed to escape into a large pipe, wherein they are condensed by a jet of water. 2000 lbs. of concentrated sulphuric acid of 1·8 spec. grav. are poured into the tank; the temperature of the mass being at the same time carefully watched by means of a thermometer, immersed in the mass, and not allowed to exceed 350° F. The heat is regulated partly by slackening the speed at which the acid is poured in, and partly by lessening the heating of the steam admitted into the tank. The admission of steam is continued throughout the operation; but as soon as the whole of the acid has been added, the fire employed for heating the steam is extinguished, and after that the admission of steam is continued for about 4 hours. The steam is heated, after it leaves the boiler, by passing through pipes placed over a fire. At the expiration of 4 hours the steam is shut off, and a large pump introduced through a pipe in the cover of the tank; then, as soon as the vapours given off will allow the pump to work, the product is pumped into a wooden vessel, lined with lead, and provided with a steam-worm; in this vessel the fatty matter is washed, by means of free steam, with about half its bulk of water, for 2 hours, and is then allowed to rest for 12 hours.

The product thus obtained can be made into soap in the ordinary manner, either alone or combined with softer and cheaper materials; but the patentees prefer to distil the product before applying it to the manufacture of soap. A cheap soap may be made by subjecting the distilled product to pressure, and employing the liquid that runs from the press for manufacturing soap, combined with about one-fourth of its weight of the substance known as vegetable wax: or it may be used for making soap in the same manner as tallow oil; the hard product remaining in the press is applicable to the manufacture of candles.

A black sediment, heavier than water, is formed in the tank in which the sulphuric acid is combined with the fatty matter; this the patentees prefer to distil in a cast iron still, into which steam is admitted, and to re-distil the product in the manner mentioned with reference to the distillation of the bulk of the acidified fatty matter; and the re-distilled product may be used for making soap.

The proportion of acid above mentioned may be increased, but with a great loss of fatty matter; and the patentees also state, that half the above proportion will give a good product for soap-making.
—Sealed Oct. 10, 1835.

THE CHEMICAL GAZETTE.

No. LXXXVII.—June 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Presence of Carbonates in the Blood.

By Prof. R. F. MARCHAND.

IN a previous investigation of the salts contained in the human blood, I found a quantity of carbonic acid equivalent to about one-half to three-fourths per cent. carbonate of soda*. Enderlin, in his researches on the composition of the ashes of the blood†, has come to the opposite conclusion, asserting that they contain no carbonates, that no such salts are contained in the blood, and that its alkaline reaction, as well as that of the ashes, is solely caused by the tribasic phosphate of soda $3\text{NaO P}^2\text{O}^5$. On this occasion Enderlin states, that "we must further conclude, from the presence of the tribasic phosphate of soda in the ashes, that the basic phosphate of soda of earlier chemists in the blood is $3\text{NaOP}^2\text{O}^5$; since only this salt, even after ignition, is still tribasic, and produces the same yellow precipitate as the ordinary phosphate of soda." Further, "if the ordinary phosphate of soda, $2\text{NaO} + \text{HO, P}^2\text{O}^5$, occurred in the blood, the ashes should contain bibasic phosphate (pyrophosphate), because the third atom of base escapes on ignition‡." And again, "if the ashes of blood be left exposed for several hours to a moist atmosphere, and a little acid be subsequently poured over them, a slight effervescence occurs. The basic phosphate of soda becoming converted, in moist air containing carbonic acid, partially into carbonate of soda, $3\text{NaO, P}^2\text{O}^5$ becomes $2\text{NaO} + \text{HO, P}^2\text{O}^5$ and NaO, CO^2 . The third atom of fixed base is replaced by 1 atom of a volatile base (HO). On ignition, the carbonic acid is again expelled with the water, and we have $3\text{NaO, P}^2\text{O}^5$." Lastly, "the behaviour of the serum of the blood towards carbonic acid gas, as well as all the phenomena of the process of respiration, are fully explained by the presence of tribasic phosphate of soda in the blood. Both the phosphates $2\text{NaOHO, P}^2\text{O}^5$ and $3\text{NaOP}^2\text{O}^5$ are remarkable from their property of absorbing a quantity of carbonic acid."

* Lehrbuch der Physiolog. Chem., p. 226.

† Chem. Gaz., vol. iii. p. 229.

‡ "In fact I have recently several times found bibasic phosphate of soda in the ashes of the blood and flesh of various animals; in this case the ashes exhibited a slighter alkaline reaction."

From the facts which Henderling discovered, and which every one who has examined ashes of the blood will have confirmed, it is however impossible to come to a direct conclusion as to the salts contained in the blood not reduced to ash, as that chemist however has done.

In my analysis of the salts of the blood, the blood was evaporated to dryness, and retained for a considerable time at 284° to 320° , then exhausted with water, and the substances dissolved in this aqueous extract determined. The insoluble mass was exhausted with muriatic acid, and this extract likewise submitted to analysis. The insoluble residue still remaining was reduced to ash, which was likewise analysed after deducting the peroxide of iron, which was added to the blood-red only. My analyses, which were made more than six years ago, cannot be considered as analyses of the ashes of blood.

It is readily perceived that, from the composition of the ashes of the blood and of organic bodies in general, no direct conclusion can be made as to the salts contained in the organic substances themselves. The circumstance that no carbonates were found in the ash does not prove in the least that they are not contained in the blood; just as little are we justified, because we find the tribasic phosphate of soda in the ash, in admitting unconditionally that it is likewise contained in the substance. This does not apply to the blood alone, but just as much to seeds and other vegetable substances*.

The proteine compounds of the blood contain sulphur and phosphorus. If they are reduced to ash, and any carbonate of soda is at the same time present in the substance, it must necessarily be decomposed, and sulphate and phosphate of soda formed. If we admit that this does not happen, and that the sulphur and phosphorus act in some other way, we must nevertheless not be astonished to meet with no alkaline carbonates in the ash. Supposing bibasic phosphate of soda to be contained in the blood, it would be impossible, with the presence of carbonate of soda, to detect this latter in the ash. It is scarcely necessary to observe, that bibasic phosphate of soda, ignited with carbonate of soda, is converted into tribasic phosphate, a reaction therefore which renders it impossible to determine from the ash whether the salt 2NaOHO , P^2O^5 and NaOCO^2 or $3\text{NaOP}^2\text{O}^5$ is contained in the substance.

I will finally observe, that the admission of the presence of $3\text{NaOP}^2\text{O}^5$ in the blood absolutely requires the admission of that of carbonate of soda. It has been indisputably proved that $3\text{NaO P}^2\text{O}^5$ is converted, on exposure to moist atmosphere containing carbonic acid, into 2NaOHO , P^2O^5 and NaO , CO^2 . Just as firmly is the fact established, that the blood contains several times its volume of free carbonic acid, and that we can remove this gas both from the venous and the arterial blood by mere pumping. The tribasic phosphate can scarcely exist in a liquid containing this gas in solution without being changed into bibasic phosphate and carbonate of

* The ashes of beans yield with nitrate of silver a yellow precipitate; it appears therefore as if the beans contained $3\text{NaOP}^2\text{O}^5$; but if the beans are extracted with water, a white precipitate is obtained which is soluble in dilute nitric acid.

soda, which latter must necessarily pass into bicarbonate of soda, as a very little time suffices to produce this change in a solution of $3\text{NaOP}^2\text{O}^5$ by the air of a room. If therefore only so much carbonate of soda is contained in the blood, that the amount of soda is but half that of the bibasic phosphate, the carbonate must disappear on the reduction to ash, and form $3\text{NaOP}^2\text{O}^5$. If the amount of carbonate of soda is greater, this salt is the more surely formed, and nevertheless the carbonate will entirely disappear, owing to the amount of sulphur and phosphorus in the proteine compounds. To prove the presence or absence of the carbonated alkalies in the blood, we must examine it in its natural state. Liebig has lately made some experiments which confirm those of Enderlin*. He arrived at the result, that no carbonated alkalies are contained in the blood, and that the alkaline reaction is due to phosphate of soda. Since free carbonic acid exists in the blood, this phosphate must be $2\text{NaO}, \text{HOP}^2\text{O}^5$; and how is it possible that $3\text{NaOP}^2\text{O}^5$ can be formed on the reduction to ash in the absence of carbonate of soda?

It does not follow, as Liebig supposes, that because muriatic acid produces no perceptible disengagement of carbonic acid from a liquid, that this contains no carbonates, since the eliminated acid may remain dissolved in the liquid, and the more so if it contain a substance in solution which has a tendency to absorb carbonic acid. The following experiments will serve to illustrate this more fully.

4.5 grms. NaO CO^2 were dissolved in 450 cubic centimetres water. 100 cub. centim. of the solution were mixed over mercury with sufficient muriatic acid to decompose the whole of the carbonate. After a considerable time and some shaking, 60 cub. centim. of carbonic acid (measured at 32° and 29.9 Bar.) were found to have been disengaged. This amounts to about 118 milligrammes. If the entire quantity contained in the liquid had been disengaged, 415 milligrammes ought to have been evolved.

3.5 grms. NaO CO^2 were dissolved in 550 cub. centim. water, 100 cub. centim. of the solution, decomposed in the same manner, liberated 11.5 cub. centim. carbonic acid, therefore about 22 milligrms. The solution contained 636 milligrms. carbonate of soda, therefore 264 milligrms. carbonic acid; of this eleven-twelfths remained in the solution, and only one-twelfth escaped as gas.

Upon this, 0.318 grm. carbonate of soda was dissolved in 100 cub. centim. water, and decomposed by hydrochloric acid over mercury. The quantity of gas given off was scarcely measurable, although the liquid contained 132 milligrms. carbonic acid. It should moreover be observed, that the barometer stood in the first experiment at 29.0, in the second at a pressure of 25.1, and the third at a pressure of 23.6, the temperature being 50° . When therefore less carbonate of soda is contained in the liquid than in the third experiment, no evolution of gas will be perceived on the addition of hydrochloric acid.

When a liquid contains along with the carbonated alkali bibasic phosphate of soda ($2\text{NaOHO}, \text{P}^2\text{O}^5$), the evolution of gas will be still

* See Chem. Gaz., p. 94 of the present volume.

more difficult to perceive, as this salt has a very great tendency to absorb carbonic acid.

The concentrated solution of the salt of 1.046 spec. grav. absorbed at 54° and 29.6 Bar. about 3 times its volume of carbonic acid, for 6.5 cub. cent. solution took up 21.2 cub. centim. carbonic acid; 100 vols. solution absorbed therefore 326 vols. carbonic acid. From this result it was to be expected that a mixture of phosphate of soda and a solution of the carbonate would essentially diminish the evolution of gas by hydrochloric acid.

100 cub. centim. solution of carbonate of soda containing 0.636 grm. salt, or 0.264 carbonic acid, were mixed with 30 cub. centim. of a saturated solution of phosphate of soda, and then decomposed with hydrochloric acid. There was now evolved, with a pressure of 25.9, 3 cub. centim. carbonic acid, therefore at 32° and 29.9 Bar., not quite 2.5 cub. centim., while the same quantity had previously liberated 11.5.

I think these experiments sufficiently prove that it is not safe to conclude on the absence of carbonates, because no evolution of gas is perceptible.

The quantity of carbonic acid which is absorbed by the solution of the phosphate of soda is more considerable than we should expect from analogy with the capacity of absorption of other saline solutions of equal density. De Saussure found that a solution of alum of 1.047 spec. grav. absorbed only 70 vols. carbonic acid to 100 vols. solution. It is therefore not improbable that the affinity of the carbonic acid to the phosphate of soda is an entirely peculiar one, and different from that towards other salts, by which it is absorbed quite mechanically. When the solution, saturated with carbonic acid, is evaporated at 104° , the crystalline mass disengages a little carbonic acid with dilute sulphuric acid.

When a concentrated solution of the phosphate of soda, 2NaOHO , P^2O^5 , perfectly saturated with carbonic acid, is placed under the air-pump, scarcely any evolution of carbonic acid is found to take place on exhaustion when the barometer has fallen to 8 inches. A few bubbles ascend along the side of the vessel, but the gas escapes in large bubbles only when the barometer has fallen below 1".

The great resemblance which exists between this behaviour, that of the blood, and that of the bicarbonate of soda, and the difference between other solutions containing gas, is rendered more evident by the following simple experiment:—4 beakers of equal size were placed under the bell-glass of an air-pump; they were filled to the same height with beaten blood, a concentrated solution of bicarbonate of soda, phosphate of soda and chloride of sodium. The last two were completely saturated with carbonic acid. The exhaustion proceeded slowly, so that the state of the barometer could be observed during the whole time. With the first strokes of the pump the gas escaped from the solution of chloride of sodium, and at 8 inches this formed a strong effervescing liquid, while in the blood and in the solution of phosphate of soda scarcely any bubbles of gas ascend. The bicarbonate of soda exhibits not the least evolution of gas. On

stronger exhaustion, the solution of chloride of sodium quite boils, if it has not already lost too much gas from the duration of the experiment. At 2 inches, the blood and the solution of phosphate begin to give off bubbles, which escape abundantly at 1 inch. The bicarbonate remains unaltered, and it is only with an almost perfect vacuum that any carbonic acid is disengaged, as has been very fully shown by Rose.

The phosphate of soda, 2NaOHO , P^2O^5 , retains the carbonic acid like the blood, but like this not the whole quantity with the same force as the bicarbonate of soda, yet with far greater tenacity than any other saline solution.

I now modified the experiment with the blood in the following manner:—The mass obtained by evaporating 5 lbs. of blood in a retort were not conveyed into a tube over mercury, but into a long-necked flask, closed with a cork, through which a long funnel and a tube for conducting away the gas were inserted; this latter was fitted air-tight into a Woulf's flask, which was half-filled with a clear solution of barytes. On heating the liquid in the flask to gentle ebullition, the steam passed through the barytic solution, causing not the slightest turbidness during the course of half an hour; but on pouring dilute sulphuric acid through the funnel, and continuing the gentle boiling, a white precipitate very soon formed, which subsided in dense flakes, and after separation from the clear liquid dissolved entirely in a little hydrochloric acid, so that the precipitation could not have arisen from any sulphuric acid having been carried over. The precipitate dissolved in the muriatic acid did not reappear on the addition of ammonia; it consisted therefore of carbonate of baryta. I have repeated this experiment three times, and always with the same result; so that I think I am justified, from the above experiments, in retaining my former opinion, that carbonates do occur in the blood.—*Journ. fur Prakt. Chem.*, April 6, 1846.

On Chlorocyanilide. By AUG. LAURENT.

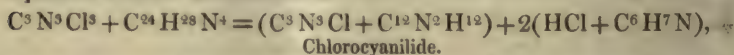
Ammonia forms two principal classes of combinations, the one usually designated by the name of *salts of ammonium*, the other by that of *salts of ammonia*. The first comprises all the salts which are formed by the union of the hydracids and the hydrated oxyacids with ammonia; the second contains the singular combinations which this alkali forms with the anhydrous acids, fluorides, chlorides, &c. It is generally admitted that the compound bodies which have served to form the latter remain after combination in their primitive state; that is to say, the sulphate of ammonia or sulphammon contains sulphuric acid and ammonia.

I have already shown, that whenever an anhydrous oxyacid combines with ammoniacal gas, there is first produced a peculiar acid, which on absorbing a further quantity of gas forms a saline compound analogous to the salts designated by the name of salts of ammonium. Thus the anhydrous sulphate and oxalate of ammonia are, in my opinion, nothing further than sulphammate and oxammate

of ammonium; it matters little whether the existence of ammonium be admitted or not.

Experiment having hitherto confirmed my theory of amidated acids, there remain to be investigated the combinations which ammonia forms with the fluorides and chlorides. Imagining that the constitution of these compounds might be more readily discovered with the aid of analogy, I examined whether aniline, which hitherto has presented so great a resemblance to ammonia, would not likewise form combinations with the chlorides and fluorides. My first experiments have been made on the solid chloride of cyanogen, and with M. Delbos on the fluoride of silicium. I intend to extend them subsequently to the other chlorides.

When the solid chloride of cyanogen is treated with aniline in the presence of water, a compound is immediately formed, which I shall call chlorocyanilide, the composition of which is entirely analogous to that which ammonia yields with the same chloride. The following equation exhibits its formation:—



i. e. 1 equiv. of solid chloride, acting upon 4 equiv. aniline, yields 1 equiv. chlorocyanilide and 2 equiv. hydrochlorate of aniline.

I have shown, in conjunction with M. Gerhardt, that when chlorocyanamide is heated, the whole of the chlorine is separated in the state of hydrochloric acid and hydrochlorate of ammonia, while mellon is left; and that when this amide is treated with potash, ammelide is formed. Chlorocyanilide, submitted to the same influences, yields results which, without being similar to the preceding, nevertheless exhibit much analogy with them. Thus, under the influence of heat, it loses all its chlorine in the state of hydrochloric acid, whilst there remains a new substance, the composition of which must be represented by $\text{C}^{15} \text{N}^5 \text{H}^{11}$. It is evident that if the chlorine had carried with it some aniline on being disengaged from the chlorocyanilide, a compound analogous to mellon would have been left.

Submitted to the action of potash, chlorocyanilide parts with hydrochloric acid, absorbs 1 equiv. water, and gives rise to a new compound corresponding to ammeline, and which is represented by the formula $\text{C}^{15} \text{H}^{13} \text{N}^5 \text{O}$. If we were to subtract 1 equiv. water, we should have the preceding compound; and if another equiv. water were added to it and 1 equiv. aniline removed, we should have a body corresponding to ammelide.—*Comptes Rendus*, April 27, 1846.

On Fluosilicanilide. By MM. LAURENT and DELBOS.

Aniline, in presence of fluoride of silicium, rapidly absorbs this gas, forming a solid apparently homogeneous substance, the composition of which may be represented by 5 equiv. aniline and 3 equiv. fluoride of silicium ($\text{F}^4 \text{Si}^2$). But the result of this combination is a mixture of hydrofluat of aniline and of a fluosilicanilide, the composition of which must be represented by $\text{C}^{24} \text{H}^{27} \text{F}^{11} \text{Si}^6 \text{N}^4$.

When this mixture is treated with alcohol of 0.86, the hydrofluante dissolves, whilst the anilide absorbs 3 equiv. of water, forming the new compound, which we have called fluosilicanilide, whose composition is represented by $C^{24} H^{33} F^{11} Si^6 O^3 N^4$.

This anilide crystallizes readily from alcohol, and notwithstanding the presence of silicium or of oxygen is entirely volatile without decomposition. Submitted to the influence of bases, it regenerates hydrofluoric acid, silicic acid and aniline.

The compounds chlorocyanilide and fluosilicanilide show that, when aniline combines with the chlorides and fluorides, there is formed, not a simple combination, but a mixture of several bodies. It is therefore highly probable that the combinations of ammonia with the anhydrous acids, chlorides, &c. are not simple combinations of ammonia, but mixtures of amides and of salts of ammonium, or rather amidated salts of ammonium.—*Comptes Rendus*, April 27, 1846.

Chemical Examination of the Bark of the Root of Laurus Sassafras.
By H. REINSCH.

The author found, in 1000 parts, 90 parts water; in the æthereal extract, a heavy essential oil, a light essential oil, and a substance resembling camphor—together, 8 parts; a substance resembling stearine, 8 parts; balsamic resin and wax, 50 parts. In the alcoholic extract—sassafrid, 92 parts; tannic acid, 58 parts. In the spirituous extract—sassafrid, tannic acid and gum, 68 parts. In the extract prepared with cold water—albumen, 6 parts; gum, red colouring principle and salts, 30 parts. In the extract with boiling water—starch, reddish-brown colouring substance, tannic acid and salts, 54 parts. In the extract with solution of potash—starch, tannic acid, &c., 289 parts; and vegetable fibre, 247 parts.

Of the two essential oils, the light one, which smelt strongly of sassafras, distilled over first; the heavy one possessed an odour intermediate between fennel and camphor, and a burning aromatic taste.

The *sassafrid* separated on treating the alcoholic extract with water; it forms, when deposited from spirit, yellowish-brown crystalline granules, rubs off like indigo, is void of odour, and has scarcely any taste. When heated in a platinum crucible, it becomes inflated, with evolution of a peculiar, disagreeable, irritating odour, and burns with a luminous flame to a cinder, which is not very easily reduced to ash. On distillation, it first melts, and then evolves a white vapour, which condenses, along with some fluid in the recipient, in the form of a white powder, which gives a greenish-blue precipitate with a solution of peroxide of iron. Nitric acid forms with it oxalic acid, and a considerable quantity of an oily body. Sassafrid dissolves but sparingly in cold water, somewhat more in water containing tannic acid, but readily in boiling, to a light reddish-brown liquid, which becomes turbid on cooling. The hot spirituous solution is of a dark reddish-brown colour, and deposits on

cooling a yellowish crystalline powder, and on the addition of water a reddish-brown amorphous powder, which on drying becomes paler. It dissolves but sparingly in æther, forming a light yellow solution. Carbonate of potash produced, in a concentrated solution of sassafrid which had been prepared with the assistance of heat, a bright red transparent liquid; ammonia the same, but gradually becoming brownish-red; it yielded with barytic water a carmine-red precipitate; with lime-water, after some time, carmine-red flakes; with chromate of potash, an abundant dark reddish-brown precipitate; with tincture of iodine, a considerable flocculent yellow precipitate; with peracetate of iron, a dark greenish-brown turbidness. Acetate of lead produced a quantity of white flakes; acetate of zinc, a slight turbidness; acetate of copper, a light brown flocculent precipitate; nitrate of silver, a faint opacity. Dilute sulphuric and nitric acid coloured the solution brighter; tincture of galls and prussiate of potash produced no alteration. According to these characters, sassafrid, which is contained in large quantity in the bark, would range near the astringent acids.

The wood of the root contains similar constituents to the bark, but in far less quantity.—*Buch. Rep.*, xxxix. p. 180.

ANALYTICAL CHEMISTRY.

On a new Method for the Quantitative Determination of Iron.

By M. H. MARGUERITE.

AMONG the various methods for the analysis of the ores of iron, there is one which is more usually employed. It consists in imitating, on a small scale, the operation carried on in the blast-furnace for the production of the metal; that is to say, the ore, after having been mixed with fluxes varying with the nature of the ore, is exposed in a crucible lined with charcoal (*brasqué*) to an intense heat long sustained. A button of cast iron is thus obtained, which indicates the richness of the ore; but it will readily be perceived that this process can hardly furnish very accurate results, for its exactitude depends on the degree of heat attained, and on the substances employed as fluxes, for the choice of which no definite rule can be laid down. It is well known moreover that the flux may occasionally retain appreciable quantities of iron, that the button may be contaminated by carbon, silicium, phosphorus, arsenic and manganese, and that numerous particles of iron may be disseminated throughout the slag.

The other analytical method, which consists in dissolving the ore in an acid, and precipitating the oxide of iron, separating it from all foreign substances, requires considerable time, especially when the ore contains phosphates, and requires a certain degree of practical dexterity on the part of the operator, which renders its employment difficult and its results uncertain. It is seldom therefore that ana-

lyses of the ores, slags, scoriæ, or the different varieties of cast iron, can be made on the spot where they are produced.

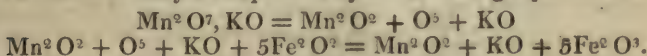
I have therefore thought that it would be useful to point out a method of estimating iron, which by its exactitude would replace with advantage the old processes, and which, on account of the ease and rapidity of its execution, might be employed by any master of an iron furnace.

The new process, which I am about to describe, is based on the employment of a normal test solution. The advantages which analytical processes founded on this principle possess are well known; it is sufficient, on this point, to allude to the determination of silver by Gay-Lussac and that of copper by Pelouze. Although the quantitative analysis of iron does not require to be made with such rigorous exactitude as those of silver and copper, which enter into the composition of monetary alloys, and others not less important, I have nevertheless endeavoured to approach as nearly as possible to the accuracy of these two processes.

The method of analysis which I propose is based on the reciprocal action of the salts of the protoxide of iron and mineral chameleon (permanganate of potash), whereby a quantity of the mineral chameleon is decomposed exactly proportionate to the quantity of iron.

Thus, in any given solution of iron at its maximum of oxidation, such as it more commonly exists in the mineral, it is only necessary to bring it to the minimum of oxidation, and then to add gradually a solution of permanganate of potash of known strength. As long as a trace of protoxide remains to be peroxidized, the colour of the chameleon is destroyed; but it is at length noticed that the colour of the last drop added is no longer destroyed, but communicates a pink tint to the whole of the solution; this reaction indicates that the operation is terminated, and the quantity of iron in solution corresponds to the amount of permanganate added.

This reaction may be expressed by the following equation:—



It will be seen that 1 equiv. of permanganate of potash is capable of peroxidizing 10 equivs. of protoxide of iron. It hardly is necessary to mention, that the solution of the iron should contain a sufficient excess of acid to hold in solution the peroxide of iron formed, and also the protoxide of manganese and potash resulting from the decomposition of the permanganate.

If now we consider the various operations in the process, we shall find they consist of the following:—

1. In dissolving the ore in an acid, hydrochloric acid for example.
2. In treating the solution of the persalt of iron which results by sulphite of soda, to reduce it to the state of protosalt, and to boil it in order to expel the excess of sulphurous acid*.

* As it is important to employ a sufficient quantity of the sulphite of soda to render the reduction of the persalt of iron to the state of protosalt complete, and yet to leave sufficient hydrochloric acid in excess in the solution, it is advantageous

3. In adding afterwards with precaution the solution of permanganate of potash until the pink tint appears, and then reading off on the graduated tube the number of divisions used.

Now it will be perceived there are two conditions to fulfill; the first, to effect a complete reduction, for the persalts of iron do not react on the chameleon; all that remained at the maximum of oxidation would escape the action of the chameleon, and consequently would not be estimated as iron; the second, to expel by ebullition the whole of the sulphurous acid in excess, which, in contact with the permanganate, would take from it the oxygen necessary to form sulphuric acid, and thus react in the same manner as the iron. But it is easily demonstrated by experiment, that the solution of a persalt of iron, treated with a sufficient quantity of sulphite of soda, is on the one hand completely reduced to its minimum of oxidation, and on the other does not contain the most minute trace of sulphurous acid after a few minutes' ebullition.

A question here naturally presents itself, whether the salts of iron, reduced to their minimum, do not absorb oxygen again with great rapidity, and thus exert an influence on the results of the analysis; the following experiment however will remove all doubts on this head. At this stage of the operation the solution was exposed to the contact of air for four hours, and the test liquor then added, a quantity of which was required exactly equal to that which was necessary when the analysis was prosecuted without any delay. This fact proves that the protosalts of iron in an acid solution are converted into persalts very slowly.

It becomes important to ascertain whether, in the ores of iron, there may not exist substances capable of reacting on the chameleon, and thus rendering the estimation of the metal erroneous.

On examining the composition of the greater number of the ores described by various authors, and particularly by MM. Berthier and Karsten, we find that they are most ordinarily composed of the following substances:—

Ores.		Metals.
Iron.	Phosphoric acid.	Cobalt.
Manganese.	Lime.	Nickel.
Zinc.	Alumina.	Titanium.
Arsenic.	Magnesia.	Chromium.
Copper.	Silica.	Tungsten.

The presence of zinc, manganese, titanium, tungsten, phosphoric acid, lime, magnesia, alumina, and silica, do not at all interfere with the accuracy of the results. Cobalt, nickel, and chrome, notwithstanding the peculiar colour of their solutions, do not in the least prevent

to use a definite and known quantity. For this purpose 250 grms. of crystallized sulphite of soda are dissolved in 1 litre of water, and a pipette which contains 10 cub. cent. is used to measure the quantity added to each assay. 2½ grms., which are contained in the 10 cub. cent. of the pipette, are more than sufficient to reduce 1 grm. of iron, but this excess is necessary to ensure the entire reduction of the persalt to protosalt.

the appreciation of the peculiar rose-pink tint of the mineral chameleon.

Arsenic and copper then are the only substances among those designated capable of producing a discrepancy in the analysis, as under the influence of the sulphurous acid the arsenic acid becomes arsenious acid, and the salts of peroxide of copper become salts of the protoxide, and afterwards withdraw oxygen from the permanganate of potash.

It is true that the ores containing arsenic are of little importance in a commercial point of view, for the iron produced from them is of so inferior a quality as to be generally rejected; nevertheless, I have considered it right to give the method of analysis in cases where it occurs, and a slight modification of the general process is sufficient.

The operation is carried on as usual, except that after having boiled the solution to expel the excess of sulphurous acid, a piece of pure laminated zinc is added, which acting upon the hydrochloric acid disengages hydrogen; arsenic and copper are hereby reduced and precipitated in the metallic state. When the solution of the zinc is complete, the solution is filtered from the precipitated particles of arsenic and copper, which would otherwise be reoxidized; and, after washing the filter three or four times with common water, the addition of the normal test liquor is proceeded with.

Preparation of the Normal Test Liquor.—There are several methods of preparing mineral chameleon. The most simple is that of Prof. Gregory. It consists in fusing together 1 atom of chlorate of potash, 3 atoms of hydrate of potash and 3 atoms of peroxide of manganese reduced to a fine powder*. The mass is afterwards mixed with so much water as to obtain as concentrated a solution as possible, to which dilute nitric acid is added until the colour becomes of a beautiful violet, and it is afterwards filtered through asbestos, in order to separate the peroxide of manganese which it holds in suspension. In this state the permanganate may be employed in the analysis. I have described the method of preparing mineral chameleon for those who have no opportunity of procuring it ready-made; but it is well to mention that it is always to be met with among the chemical manufacturers, and I now employ the chameleon procured from this source.

The permanganate of potash is a preparation of great stability, and may be preserved for a very long time without undergoing any alteration, provided it be defended from the contact of organic matters and kept in a glass-stoppered bottle. To convert its solution into a test liquor of known value, 1 grm. of pure iron, such as harpsichord wire, is dissolved in about 20 cub. cent. of strong hydrochloric acid, free from iron; after the disengagement of the hydrogen has

* Or KOClO_5 , 7 parts; KOH , 10 parts; MnO_2 , 8 parts. The manganese should be in the finest state of division possible; the potash, dissolved in water and mixed with the other substances, dried, and the whole heated to very dull redness for 1 hour. By attending to these precautions, the preparation is sure to succeed.—*Ed. Chem. Gaz.*

ceased and the solution is complete, the liquid is diluted with about 1 litre of common water*.

The solution of permanganate of potash is then added, drop by drop, until a slight pink colour is manifest, and the number of divisions on the tube necessary to produce this effect carefully noted; this number is then employed to reduce into weight the result of an analysis of an ore.

When the solution of chameleon is too concentrated, it is easy, by adding the proper quantity of water, to reduce it to one-half, one-fourth or one-fifth, so that 30 cub. cent. shall be as nearly as possible equivalent to 1 grm. of iron.—*Comptes Rendus*, No. xiv.

New Test for Prussic Acid.

The following new method of testing for hydrocyanic acid is proposed by Mr. Richard Austin, jun., of this city. The precipitate of cyanide of silver, say $\frac{1}{2}$ gr., obtained in the usual manner, is mixed with a small quantity of oxide of iron and carbonate of potash, and the whole fused together in an iron or platinum capsule. The fused mass is then dissolved in $\frac{1}{2}$ oz. of distilled water, filtered, and rendered slightly acid by the addition of a few drops of hydrochloric acid. The liquid thus treated is next divided into two portions, to one of which a few drops of a solution of sulphate of copper is added, which immediately causes the evolution of the chocolate-brown colour, so characteristic of the ferrocyanide of copper; and to the other a few drops of the muriate tincture of iron, or any persalt of iron, when the solution becomes intensely blue by the formation of the ferrocyanide of iron, the ordinary prussian blue.

In Mr. Austin's opinion, "these two tests, with the well-known odour of prussic acid, are, *independent of all others*, sufficient to convince the medical jurist of the presence of free prussic acid." Mr. Austin adduces several arguments to show the superiority of this test over those already known to chemists, both in accuracy and facility of application, by persons not skilled in chemical manipulation.

The precipitates above mentioned are very distinctly obtained with $\frac{1}{2}$ gr. of cyanide of silver.—*Dublin Hospital Gazette*.

Method of detecting very minute Quantities of Copper in Organic Fluids. By M. FILHOL.

A very delicate test consists, according to Virgain†, in immersing a piece of metallic iron in the fluid contained in a platinum crucible, when the copper is deposited on the platinum, and may then be dissolved with a few drops of nitric acid. The author proposes the following modification of this method:—He acidifies a large quan-

* It is necessary to use solutions very dilute and cold, in order to prevent the hydrochloric acid in excess from reacting on the chameleon and disengaging chlorine.

† Chem. Gaz., vol. i. p. 14.

tity of the fluid under examination in an evaporating dish, and then immerses in it a piece of platinum foil surrounded by a small zinc plate, when the copper is deposited on the platinum, colouring it red, and can be dissolved with a few drops of nitric acid.—*Journ. de Med. et de Chim. de Toulouse*, ix. p. 78.

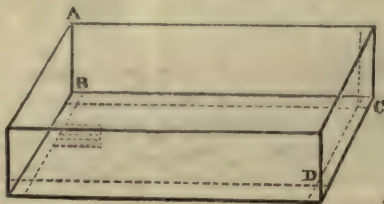
On the Precipitation of some Metals with Sulphuretted Hydrogen.
By Dr. VOGEL.

In precipitating lead with sulphuretted hydrogen, it is usual to warm the liquid to prevent any of the precipitate passing through the filter; this, the author has found, may give rise to considerable loss. If sulphuretted hydrogen be passed through a moderately strong solution of acetate of lead until the filtered liquid contains no more lead, and is consequently not rendered turbid either by sulphuretted hydrogen or by sulphuric acid, and the liquid be now warmed, a further precipitate is produced by sulphuretted hydrogen after filtration. The liberated acetic acid evidently decomposes the sulphuret of lead. It is the same with the nitrate of lead, and remarkably so with the chloride. This is of considerable importance where lead has to be separated from chlorides, and cannot however be precipitated with sulphuric acid. With mercury and bismuth no such decomposition of the sulphurets occurs, and with antimony only in a slight degree. The above behaviour may even be employed for the separation of some metals. If, for instance, sulphuretted hydrogen is passed into a liquid containing nitrate of bismuth and nitrate of lead until no further precipitate results, and the whole be then heated to boiling, the sulphuret of lead is wholly redissolved, while the sulphuret of bismuth is not attacked. The lead may then be precipitated by sulphuric acid from the solution.—*Buch. Rep.*, xli. p. 360.

Description of a new Mercurial Trough.
By Professor LOUYET of Brussels.

In small laboratories, in which one of the chief points to be aimed at is œconomy, in making researches on gases soluble in water, a small porcelain trough is commonly employed capable of containing 20 to 25 lbs. of mercury. The size of the bell-glass is proportioned to the capacity of the trough; thus only small quantities of gas can be collected—quantities often insufficient for the desired experiments. With a view to obviate this inconvenience, I have modified the mercurial trough, so as to be able, without sacrificing œconomy, to collect considerable quantities of gas; and I have thought it may be of use to give a description of this new instrument, for the service of persons engaged in particular researches. This apparatus is formed of a small oblong oak box, to the bottom of which is cemented a glass, which fits exactly over its whole extent. The external surface of this glass is carefully polished and prepared. In the centre of one of its small sides (it is rectangular) is worked a

narrow and deep groove parallel to the large sides of the right angle. This opening corresponds to a hollow in the bottom of the box. This being done, I arrange the apparatus in the following way, when I desire to collect a gas over mercury:—I procure bell-glasses made of emery-stoppered bottles, the bottom of which is removed; the edges of these receivers are prepared and rubbed with emery, and apply accurately to the ground glass, precisely like the receiver of an air-pump. The edges may be very slightly greased, or this precaution may be dispensed with. The receiver is placed on the ground glass, which is kept fixed with one hand; with the other hand the stopper is removed, and it is entirely filled with mercury; then it is carefully re-stoppered. This being done, a small quantity of mercury is poured into the box, so as to fill the small cavity and to cover its bottom with a thin stratum. The receiver may now be moved in all directions, and may be slid until it is over the small cavity, into which the extremity of the curved tube by which the gas is disengaged is adapted. To one of the angles of the box may be fitted a small pure iron stop-cock, by which the mercury is drawn off when the operation is ended. For greater clearness, I subjoin a figure, which represents this new trough of the dimensions which I have adopted.



AB = $4\frac{1}{2}$ centimetres*. BC = 23 centimetres. CD = 17 centimetres.
Depth of the longitudinal groove, taken above the glass plate, = 2 centimetres.

Phil. Mag., May 1846.

CHEMICAL PREPARATIONS.

On the Preparation of Hydrosulphocyanic Æther. By M. LÆWIG.

WHEN a concentrated solution of sulphocyanide of potassium is saturated with hydrochloric æther, chloride and hydrosulphocyanic æther are obtained. The reaction takes place very slowly; the rays of the sun however hasten it. As soon as it is terminated, the liquid is diluted with its volume of water and distilled; the distilled product is then mixed with twice its volume of pure æther, and sufficient water added to separate the æther holding in solution the new

* The centimetre is equal to 0.393708 of an English inch.

hydrosulphocyanic æther. These two bodies are separated by distillation, and the latter rectified over chloride of calcium.

Hydrosulphocyanic æther forms a colourless liquid, with highly refractive powers, tastes like aniseed, and has a penetrating odour similar to that of mercaptan. At 59° it has the same density as water; it likewise boils at about 212° . It may be boiled for some time with a solution of caustic potash without decomposition resulting; but with a boiling alcoholic solution it disengages ammonia as well as bisulphuret of ethyle. On evaporating the alcoholic solution, a considerable quantity of carbonate of potash is obtained, without any trace of sulphocyanide. If however an alcoholic solution of sulphuret of potassium be mixed with this æther, there is produced, especially on the application of heat, sulphuret of ethyle and sulphocyanide of potassium. The presence of this latter is proved on evaporating the liquid, and dissolving the residue in water, which then gives the characteristic reaction of the sulphocyanides with persalts of iron.

The alcoholic solution of the new æther is not precipitated by metallic solutions. Nitric acid decomposes it with violence, but only a very small quantity of sulphuric acid is formed. It contains, according to M. Löwig, $C^6 H^5 NS^2$.—Poggendorff's *Annalen*, lxxvii. p. 101.

On the Preparation and Properties of Angelic Acid.
By L. HOFFMANN and H. REINSCH.

Angelic acid was first described by Buchner, jun., in 1842, and recently it has been examined by Meyer and Zenner*. The authors have likewise devoted their attention to this subject. They extracted 8 lbs. of good coarsely-pounded *Angelica* root three times with spirit of 0.863 spec. grav. and the assistance of heat, pressed the residue, and removed the spirit from the united tinctures by distillation. The last portion which passed over possessed a strong odour and taste of *Angelica*; the residue in the retort consisted of angelica balsam and some aqueous fluid. The balsam was washed several times with water, and dissolved in a fresh concentrated solution of caustic potash; the mass which solidified on cooling contained a quantity of distinct crystals; on the application of heat, an oil of a peculiar odour passed over mixed with water; the distillate had a strong alkaline reaction; it was accurately saturated with dilute sulphuric acid, when the oil acquired a totally different odour. The oil was yellowish, and amounted to scarcely half a drachm. On opening the tubulure of the retort, a strong smell of ammonia was perceptible, however only when air was admitted; the alkaline solution of balsam was now mixed with æther, and as this would not separate properly, some water was added, in which the balsam dissolved while the æther separated. On evaporating the latter, laminar crystals are obtained, especially when a little alcohol has been added.

* See page 129 of the present volume.

This substance, which Buchner calls *angelicine*, was extremely light and of a satiny lustre, but in other respects possessed all the properties assigned to it by Buchner. The alkaline liquid, freed from æther, was mixed with 8 vols. of alcohol of 0.833 spec. grav., and set aside for 24 hours, when a resinous substance was deposited in flakes; the dark brown solution was freed from spirit and neutralized with sulphuric acid until the whole of the resin appeared to be precipitated, and the liquid had an acid reaction. It was then cautiously submitted to distillation, when a water passed over which had a peculiar smell, but not that of angelicic acid. The residue in the retort consisted of a brown resin and a small quantity of a clear reddish-brown liquid. Mixed in a test-tube with an excess of dilute sulphuric acid, it yielded a white turbidness, evolved a strong odour of acetic acid, and a quantity of acicular crystals of angelicic acid were deposited on the sides of the glass. The red liquid in the retort was therefore decanted from the resin, the latter again exhausted with boiling water, and the united liquids saturated with sulphuric acid and distilled. A clear acid water passed over, upon which floated drops of oil, which however had already become partially converted in the neck of the retort into crystals more than an inch in length. The acid thus obtained still possessed a yellowish colour and a faint empyreumatic odour, as well as the odour of acetic acid and a burning taste. Placed on the tongue, it produced a white spot. The aqueous distillate was heated nearly to boiling, and saturated with a solution of carbonate of soda. On evaporation, the reaction of the solution again became alkaline, and an acid water of a peculiar odour again distilled over. As the angelicate of soda would not crystallize, it was treated with alcohol, when carbonate of soda separated. After some days the spirituous solution deposited crusts of crystals of a faint odour of cinnamon, remarkably sweet taste and slightly alkaline reaction. A portion of the angelicate of soda was left to spontaneous evaporation along with free angelicic acid; however, no crystals separated until some spirit was added. These crystals possessed a less sweet but more warming aromatic taste and a neutral reaction; they yielded with acetate of lead a turbidness, which always redissolved. When so much of it had been poured into a solution of acetate of lead that the precipitate no longer disappeared, the liquid was warmed, which caused it to dissolve; in the course of 12 hours some warty crystals had separated. Acetate of copper gave a bluish-white, nitrate of silver a white precipitate; but after some hours metallic silver separated. Protonitrate of mercury yielded a white precipitate, which again dissolved without any reduction taking place. No precipitate was produced in a solution of the perchloride of mercury; but after 24 hours a yellow basic salt had separated, and in the upper part of the tube needles of angelicic acid. Chloride of platinum was not altered, nor was tartar-emetic and sulphate of zinc. Peracetate of iron gave a yellowish-brown precipitate, which appeared to be soluble in water.

To prepare a combination of the acid with the oxide of ethyle, a mixture of 1 part concentrated sulphuric acid with 2 parts alcohol

of 0.80 spec. grav. was distilled with angelicate of soda in a retort at a very gentle heat, when the æther distilled over in oily stripes. After separation, by means of water and chloride of sodium, it is colourless, possesses a peculiar odour, calling to mind that of rotten apples, greatly excites coughing, has an aromatic sweetish taste, burns with a bluish flame, and stupifies. The authors suffered from violent headache in its preparation.

To shorten the above very circuitous method of preparing the acid, the authors mixed an ounce of angelica balsam with the same quantity of hydrate of lime, melted the mass, exhausted it with boiling water, saturated with sulphuric acid and distilled. They however recommend, as still more simple, the process followed by Meyer and Zenner.—*Jahrbuch für Prakt. Pharm.*, xi. p. 217.

Observations on Myrrh and on a Method of distinguishing it from Bdellium. By L. F. BLEY and E. DIESEL.

The extremely different amount of essential oil obtained from myrrh, varying between 3.60 and 3.10 per cent., depends, according to the authors' observations, on the oxidation of the essential oil. Myrrh, which contains but little of this oil, always exhibits a strongly acid reaction, which is never found in that containing a greater proportion. Humidity especially favours the oxidation, and the moistening myrrh with alcohol to give it a better appearance should be entirely dispensed with. In the preparation of the essential oil, the water freed from the oil is found to have a strong acid reaction. This was saturated with carbonate of lime mixed with acetate of lead, evaporated, and treated with absolute alcohol, when formiate of lead was precipitated. This salt was decomposed by means of phosphoric acid, and the presence of the formic acid confirmed by the tests with perchloride of mercury and perchloride of iron. The essential oil of myrrh gradually acquires an acid reaction by exposure to the air, becoming at the same time thickened to a turpentine-like mass. The residuary balsam-resin dissolves readily in æther, alcohol and oil of turpentine, has at first a slight, subsequently a strong bitter taste, and melts readily on the application of heat. The oil of myrrh is probably a carburetted hydrogen of similar constitution to the oil of turpentine. Benzoic acid is said by Brandes to occur in myrrh; the free acid, however, which he considered to be benzoic acid, appears to be nothing more than formic acid.

Pseudo-myrrh, which has been frequently found mixed with the genuine myrrh, consists of large pieces of different forms, the majority of them seeming to be fragments of a cylindrical body; they are coated externally with dust, and have a dirty reddish-brown colour; the surface of fracture is tolerably even, of vitreous lustre, brownish-yellow colour, and nearly as transparent as Senegal gum. It has a faint myrrh-like odour, and a disagreeable bitter, somewhat balsamic taste. Nitric acid dissolves it to a bright yellowish liquid, from which water separates small yellowish particles. Genuine myrrh yields with nitric acid a transparent dirty yellow liquid. *Bdellium*

indicum is not dissolved by nitric acid ; it softens, becomes whitish and opaque. Bibulous paper, moistened with the alcoholic extract of myrrh and then with nitric acid, acquires the blood-red colour first observed by Bonastre ; *bdellium* and pseudo-myrrh exhibit only a yellow or brownish colouring. *Bdellium indicum* is moreover distinguished by its greenish-brown colour, its more terebinthinate odour, and bitter and somewhat acrid taste. It becomes viscous when held for some time between the fingers. Myrrh yields a bright golden yellow tincture and an opaque whitish residue ; pseudo-myrrh, a light yellow tincture and a semi-transparent residue ; *Myrrha indica*, a dark yellow tincture and an opaque residue. An addition of water produces in the first and last a milky turbidness, and in the second no change. Nitric acid (6 drops to 20 of the tincture) yields with *M. electa* a yellowish-white opacity, upon which after a time the periphery of the liquid acquires a bright violet colour, while the centre remains yellow. *M. indica* behaves similarly, only that the colour is darker ; pseudo-myrrh does not exhibit this reaction. Fuming nitric acid produces with the tincture of *M. electa* an amber-brown, and finally a dark violet colour ; on evaporation, a dark gamboge-coloured residue is left ; *M. indica* exhibits the same reaction ; pseudo-myrrh experiences no change. *Bdellium indicum* and *africanum* are distinguished by their not assuming a violet colour on their treatment with nitric acid. About 10 grs. of myrrh, shaken with an ounce of water and filtered, yield with solutions of salts of the oxide of lead a considerable precipitate. *Bdellium indicum*, treated in the same manner, exhibits scarcely any opacity.—*Archiv der Pharm.*, xliii. p. 304.

PROCEEDINGS OF SOCIETIES.

Royal Society.

April 2, 1846.—Contributions to the Chemistry of the Urine. Part II. "On the Variations in the Alkaline and Earthy Phosphates in Disease." By Henry Bence Jones, M.D.

The analyses, of which the results are given in a series of tables, were made by the author, chiefly from the urine of patients labouring under different diseases in St. George's Hospital, and therefore nearly under the same circumstances as far as exercise was concerned. He found that the variations in the earthy phosphates were in general independent of the nature of the disease. In fractures of the spine and paraplegia, however, the total amount of these salts was slightly above the healthy standard during the early period, and when inflammatory action might be considered as prevailing ; but when this action had subsided, and the affection had become chronic, the total quantity of phosphatic salts was less than natural. In chronic diseases of the brain, and in chronic and even in acute diseases of the membranes, no increase of these salts was observed.

In fractures of the bones of the skull, when inflammation of the brain supervened, there was a slight increase of the total amount of phosphates; but no such increase occurred when the head was not affected, even although acute inflammation of other organs existed. In acute inflammation of the brain there was an excessive secretion of phosphates, which returned to the natural quantity as soon as the inflammation passed into the chronic state. In some functional diseases of the brain, attended with delirium, the secretion of the salts was excessive; but the excess ceased with the disappearance of that symptom. In other functional diseases, as in fevers, no excess was observable. In delirium tremens, when food could be taken, there was neither excess nor deficiency; but in the most violent cases, where no food could be taken, the quantity of the phosphates was diminished in a most remarkable degree. In the general paralysis of the insane, no increase of phosphates was observed. One case of acute paroxysm of mania showed a small increase during the paroxysm; in two other cases of mania there was a diminution of phosphates approaching to that occurring in delirium tremens. Bright's disease, even attended with acute inflammation, showed no increase. When only a few ounces of urine were secreted, as in dropsy, no increase was observed; and none also in a very extreme case of exostosis. In the case of mollities ossium, there was a decided increase of the earthy phosphates; and at last, the alkaline phosphates were also in excess, although there was no indication of affections of the nervous structures.

The following are the general conclusions which the author draws from his inquiries: first, that acute affections of the nervous substance, organic and functional, are the only diseases in which an excess of phosphatic salts appears in the urine; and in acute inflammation of the brain, its amount is proportional to the intensity of the inflammation; secondly, that in a large class of functional diseases of the brain, of which delirium tremens presents the most marked example, the secretion of phosphates is most remarkably diminished; and lastly, that no chronic disease exhibits any marked excess in the total quantity of phosphatic salts secreted, at least as far as the mode of analysis employed by the author can be regarded as conclusive.

Chemical Society of London.

April 20, 1846. (The President, Professor Graham, in the Chair.)

"On the Constitution of Aqueous Solutions of Acids and Alkalies," by Mr. J. Griffin.

After alluding to the researches of Dalton on the subject of atomic volumes, and reviewing the paper of Messrs. Playfair and Joule, published in the Society's 'Transactions,' vol. ii. pp. 401-481, the author states, that in the course of an inquiry on centigrade testing, he examined the constitution of a great number of solutions of the principal acids and alkalies, and found that the results were at variance with the doctrines laid down by the above-mentioned expe-

rimenters. Mr. Griffin finds only one substance, ammonia, that appears to have a fixed atomic volume in solution in water; the others vary constantly, according to their state of dilution. The method of conducting these investigations, with a description of the measures used, and a statement of the researches made on the subject, is then detailed; and the large series of results arising are, as far as possible, thrown into a tabular form. No less than twenty tables are thus obtained, entitled,—1st, on water; 2nd, on sulphuric acid; 3rd, showing the increase of specific gravity occasioned in solutions of sulphuric acid by condensation; 4th, muriatic acid; 5th, showing the increase of specific gravity occasioned in solutions of muriatic acid by condensation; 6th, nitric acid; 7th, increase of specific gravity occasioned in solutions of nitric acid by condensation; 8th, acetic acid; 9th, increase of specific gravity occasioned in solutions of acetic acid by condensation; 10th, anhydrous potash; 11th, increase of specific gravity in solutions by condensation; 12th, carbonate of potash; 13th, soda; 14th, carbonate of soda; 15th, ammonia 1; 16th, ammonia 2; 17th, ammonia 3; 18th, sal-ammoniac; 19th, sugar; 20th, sulphate of magnesia. Each of these tables is followed by copious explanations and remarks, which afford a compendium of much valuable and interesting matter to the manufacturer as well as the scientific chemist.

“On the Maximum Density of Water,” by Messrs. Joule and Playfair.

In this the authors contended that the point of maximum density is the proper standard at which water should be taken as unity for the purpose of comparing specific gravities. There are two methods for determining the point of maximum density of water; one of these being the comparison of water in its expansion with that of some other substance the expansion of which had been already determined; the other virtually consists in weighing water in water, and was pursued by Hope in his original researches on this point. The authors adopted the latter method as the one most likely to yield correct results, but altered the method of experimenting and the nature of the apparatus employed. Their apparatus consisted of two vessels connected at the bottom by a pipe with a cock, above by an open canal. One of these vessels was made to contain water at a temperature decidedly below that of the maximum density, the other being above that temperature. On opening the stop-cock, a current took place from the colder vessel to the hotter, until a certain time, when the current became reversed. The rapidity and direction of the current was determined by hollow glass beads. The experiment was tried under varying conditions; and, as a mean of several series of experiments, the authors fixed 39.101° F. as the point of maximum density, stating that they believed this to be within one-hundredth of a degree of the truth; at all events, that it could not be one-twentieth of a degree in error.

THE CHEMICAL GAZETTE.

No. LXXXVIII.—June 15, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Analyses of the Ashes of Plants.

[In the following article we have collected together a number of analyses of the ashes of plants which have recently been made by several chemists, principally under the direction of Dr. H. Will of Giessen. As this subject is at present engaging considerable attention, from the importance attached to it in an agricultural point of view, we have no doubt it will prove interesting to many of the readers of this Journal. For the better comparison of the results, the plants have been arranged according to their position in the Natural System. We would however observe that a greater benefit is generally expected to be derived from these investigations than in our opinion is likely to result.]

Fucaceæ.—The plants analysed by Gödechens were collected on the west coast of Scotland, near the mouth of the Clyde; the *Fucus vesiculosus*, analysed by James, in the neighbourhood of Liverpool. The iodine was determined, in the former analyses, partly as iodide of palladium, and partly calculated from the difference in the weight of the chloride and iodide of silver previous and subsequent to treatment with chlorine gas:—

	Gödechens.				James.
	<i>F. digitat.</i>	<i>F. vesiculos.</i>	<i>F. nodosus.</i>	<i>F. serrat.</i>	<i>F. vesic.</i>
Potash	22·40	15·23	10·07	4·51	
Soda	8·29	11·16	15·80	21·15	15·10
Lime	11·86	9·78	12·80	16·36	16·77
Magnesia	7·44	7·16	10·93	11·66	15·19
Peroxide of iron ..	0·62	0·33	0·29	0·34	4·42
Chloride of sodium	28·39	25·10	20·16	18·76	9·89
Iodide of sodium ..	3·62	0·37	0·54	1·33	
Sulphuric acid . . .	13·26	28·16	26·69	21·06	30·94
Phosphoric acid ..	2·56	1·36	1·52	4·40	
Silica	1·56	1·35	1·20	0·43	7·69
Per-centage of ash	20·40	16·39	16·19	15·63	13·22
Chem. Gaz. 1846.					N

	Gramineæ.					
	Ash of the grains of barley.	Ash of barley.	Ash of wheat.	Straw of maize. Hruschauer*.		<i>Secale cornutum.</i> Engel- mann.
	Köchlin.	Schmidt.	Schmidt.	I.	II.	
Potash	13·75	29·91	25·90	14·46	4·78	45·38
Soda	6·75	..	0·44	39·92	12·69	16·79
Chloride of sodium	..	..	..	6·29	0·55	
Lime	2·21	1·67	1·92	4·93	11·00	1·68
Gypsum	..	..	..	1·01	1·37	
Magnesia	8·60	6·91	6·27	1·84	11·44	5·34
Alumina	..	0·83				
Peroxide of iron ..	1·07	2·10	1·33	0·90	0·73	2·34
Chlorine	..	..	..	..	..	2·36
Phosphoric acid ..	39·80	38·48	60·39	11·76	22·39	15·44
Sulphuric acid	0·17	..	..	..	..	0·02
Silica	27·65	29·10	3·37	18·89	35·05	10·65
Per-centage of ash	2·70	..	..	6·50	2·30	0·36

The barley examined by Köchlin (*Hordeum distichon*) was from Neufchatel. Erdmann observes that the mode of preparation of the ashes for analysis has great influence on their apparent composition. He burns the plant or seeds in a muffle-furnace, in which, in the course of 3 to 4 hours, from 12 to 15 grms. of the most beautiful ash of corn may be obtained. The ashes so prepared, especially in those seeds that are difficult to reduce to ash, generally contain the phosphoric acid at a lower state of saturation than those prepared in a crucible. The ash of rye, which usually contains an alkaline phosphate, yielding with oxide of silver a white precipitate, gives a yellow one when it has been prepared by long-continued ignition in a covered crucible. Biphosphate of potash, when ignited for a long time with carbonized sugar, is converted into a bibasic, and finally even into a tribasic salt. Evidently the phosphoric acid is reduced, which is also the case with the sulphuric acid†. The ashes were dissolved in muriatic acid and evaporated; the soluble residue, after separation of the silicic acid, precipitated with ammonia; the filtered solution evaporated in a platinum crucible, and exposed to a strong red heat. The ignited phosphates of the alkalies are dissolved, when some phosphate of magnesia generally remains; the solution is precipitated with acetate of lead, the filtered solution digested with carbonate of ammonia, and then evaporated to dryness with muriatic acid. The earthy salts were fused with carbonate of soda and silica, extracted with water, the residue decomposed with muriatic acid, and the earths determined individually. On dissolving the alkaline phosphates in a specimen of wheat-ash, a white insoluble mass remained, which contained but a very little magnesia. It dissolved in acetic

* I. from a soil consisting of disintegrated quartzose schist; II. grown on disintegrated transition limestone.

† As the ashes of several plants, for instance those of the *Algae*, fuse very easily, and cannot then be entirely burnt, and at the same time the sulphates are reduced to sulphurets, which cannot be wholly reoxidized by mere ignition exposed to the air, Will recommends burning them with oxide of mercury.

acid. After separation of the phosphate of magnesia, evaporation and ignition, the mass again remained as an insoluble residue; it proved to be an insoluble, or at least a very sparingly soluble modification of monobasic phosphate of potash.

The ashes of the straw of Indian corn I., examined by Hruschauer, contain more alkaline bases than those of the straw II. The plant was 6 feet high, and had borne a considerable quantity of fruit; the straw of No. II. was smaller, and had yielded but a poor produce:—

	<i>Aroideæ.</i>		<i>Cupuliferæ.</i>		<i>Ulmaceæ.</i>	
	<i>Acorus</i> <i>Calamus.</i> Rüling.		Wood of <i>Quercus</i> <i>Robur.</i> Deninger.	Seed of <i>Fagus</i> <i>sylvatica.</i> Souchay.	<i>Ulmus campestris.</i> Wrightson.	
					Wood*.	Bark.
Potash.	32·926		8·43	22·82	21·92	2·22
Soda	..		5·65	9·50	13·72	10·09
Chloride of po- tassium }	14·657					
Chloride of sodium	2·838		..	0·87		
Lime	11·479		75·45	24·50	47·80	72·70
Magnesia	7·709		4·49	11·64	7·71	3·19
Proto-peroxide of manganese . . }	1·418		..	3·11		
Peroxide of iron..	..		0·57			
Phosphate of iron	2·768		..	2·67	1·69	1·19
Phosphoric acid ..	12·341		3·46	20·81	2·81	1·22
Sulphuric acid ..	5·059		1·16	2·20	1·28	0·62
Chlorine	..		0·01			
Carbonic acid . . .	5·400					
Silica	2·398		0·78	1·88	3·07	8·77
Per-centage of ash	6·900					
	<i>Compositæ.</i>					
	Ash of the seed of <i>Madia</i> <i>sativa.</i> Souchay.	Herb and flowers of <i>Anthemis</i> <i>arvensis.</i> Rüling.	<i>Matricaria</i> <i>Chamomilla.</i>		<i>Cen- taurea</i> <i>Cyanus.</i> Rüling.	
			I.	Rüling. II.		
Potash	9·53	30·577	25·490	32·386	36·536	
Chloride of potas- sium }	..	7·152	18·493	14·257	11·880	
Soda	11·24					
Lime	7·74	16·009	19·104	16·421	15·487	
Magnesia	15·42	3·666	4·942	4·787	4·561	
Peroxide of iron ..	1·08					
Phosphate of iron..	..	4·770	2·396	2·396	2·344	
Phosphoric acid ..	54·99	9·941	5·113	7·805	6·593	
Sulphuric acid . . .	..	4·604	4·986	4·342	2·695	
Carbonic acid . . .	..	14·300	17·000	15·200	15·000	
Silicic acid	..	6·800	1·653	1·529	3·291	
Per-centage of ash	..	9·660	8·510	9·690	7·320	

* Mean of two analyses.

The corn-flower and wild chamomile I. were from a field sown with rape-seed in the neighbourhood of Giessen; the corn chamomile and wild chamomile II. were from a rye-field. The soil of the first field exhibits the composition given under A, that of the second under B:—

	A.	B.
Silica.....	85.02	68.060
Peroxide of iron	3.32	8.962
Alumina	6.20	17.920
Lime.....	0.42	0.430
Magnesia	0.14	0.133
Potash	2.84	2.952
Chlorine	Trace.	0.016
Phosphoric acid ..	Traces.	Traces.
Sulphuric acid		
Manganese		
Loss	0.06	1.527

	<i>Rubiaceæ.</i>			<i>Solanææ.</i>	<i>Scrophularinææ.</i>
	Ash of <i>Rubia tinctorum</i> from Alsatia.		Madder from Seeland.	Ash of the seed of <i>Datura Stramonium</i> .	Leaves of Purple Foxglove.
	I. Köchlin.	II.	May.	Souhay.	Wrightson.
Potash.....	29.35	26.64	3.42	20.22	43.53
Soda	15.89	11.67	25.76	14.24	3.70
Chloride of sodium ..	..	..	12.58	..	9.03
Lime	34.54	29.25	16.29	4.11	12.67
Magnesia	3.72	3.68	3.17	17.56	6.35
Peroxide of iron..	1.18	3.36	2.67	3.94	4.63*
Phosphoric acid ..	5.26	4.62	16.84	34.72	0.44†
Chlorine.....	4.71	13.25	..	..	6.69†
Sulphuric acid ..	3.68	2.14	2.86	..	12.78
Silica	1.64	5.36	16.41	5.21	100.00
	100.00	100.00	100.00	100.00	100.00
Per-centage of ash	8.25	8.42	..	..	10.89

For the analysis made by Köchlin of the madder-root, very strong and healthy specimens were employed; that under I. grew on a calcareous soil, that under II. on a soil containing much less lime. The leaves of *Digitalis purpurea* contain, according to Wrightson, a large amount of nitrogen; they yielded, after deducting the ash, 6.80 per cent. The ashes of *Atropa belladonna* contain 8.64 per cent. chlorine and 6.28 nitrogen. *Conium maculatum* likewise contains a large amount of nitrogen and chlorine:—

* Phosphate of iron.

† Lime salts.

Umbelliferae.

Leaves of

*Conium**maculatum.*

Wrightson.

Ampelideae.

Ash of the vine.

		Hruschauer.			Crasso.
		I.	II.	III.	
Potash.....	21.69	43.13	24.93	26.41	37.482
Soda	9.64	7.59	7.00	8.57	1.336
Chloride of sodium	16.61	0.83	0.58	0.41	1.614
Lime	14.96	30.28	35.94	31.78	34.344
Magnesia	8.39	4.66	7.12	9.16	1.055
Phosphate of lime	16.77	..	..	..	15.694
Gypsum	5.88	4.55	4.02	4.13	6.186
Peroxide of iron..	3.49*	0.16	0.24	0.19	1.564*
Phosphoric acid..	..	16.35	19.55	16.87	..
Silica	2.62	1.45	0.62	2.48	0.725
Per-centage of ash	..	..	..	..	2.849

The vines examined by Hruschauer were from Lower Styria; I. from *débris* of quartzose rocks (formed by the decomposition of gneiss, micaceous schist, clay slate, chlorite, hornblende, quartz, and a little lime); No. II. from decomposed transition limestone, and No. III. from micaceous schist. The ashes contained predominantly bibasic phosphates, and at the same time tribasic. Crasso employed for his analysis vines of one and two years' growth, from the neighbourhood of Meissen, which had grown on a soil formed by the decomposition of porphyry, and which contained but very little vegetable mould. The burning was made in a platinum crucible, as some of the constituents of the ashes appeared to be volatilized in the muffle. On comparing the quantity of the ash of the highly developed pith with that of the wood, the author found in the former, I. 4.81, II. 4.80 per cent.; in the latter, I. 2.45, II. 2.49 per cent.; so that the pith contains twice as much inorganic constituents as the wood. The juice of ripe grapes yielded 0.326 per cent. ash; the juice of unripe grapes, 0.371 per cent.:

Cruciferae.

Ash of mustard seed.

James.

Papaveraceae.

Ash of

*Chelidonium**majus.*

Rüling.

Caryo-
phyllæ.

Ash of

*Agrostemma**Githago.*

Rüling.

	James.			
	White.	Black.		
Potash.....	10.02	12.66	33.111	22.865
Soda	9.61	4.09	..	..
Chloride of potassium	..	..	3.398	7.554
Chloride of sodium..	..	2.27	..	..
Lime	21.28	17.34	23.372	26.266
Magnesia	11.25	14.38	5.065	6.146
Peroxide of iron...	1.46	1.12	1.800*	1.800*
Phosphoric acid	37.41	37.39	15.107	6.649
Sulphuric acid.....	5.41	7.17	2.248	2.387
Carbonic acid	..	..	14.200	18.600
Chlorine	0.20	..	..	..
Silica	3.36	2.78	1.410	2.389
Per-centage of ash ..	4.15	4.31	6.850	13.200

* Phosphate of iron.

	<i>Tiliaceæ.</i>		<i>Aurantiaceæ.</i>	<i>Pomaceæ.</i>
	Ash of pine-tree.		Ash	Ash
	Hoffmann.		of	of
	Bark.	Wood.	lemon pips.	quince pips.
			Souchay.	Souchay.
Potash	16·144	35·802	33·89	27·09
Soda	4·529	5·235	3·56	3·01
Chloride of sodium..	2·288	1·491	2·31	2·57
Lime	60·811	29·930	12·87	7·69
Magnesia.....	8·035	4·147	8·67	13·01
Peroxide of iron	1·237	7·975	0·24	1·19
Phosphoric acid	4·017	4·849	34·81	42·02
Sulphuric acid.....	0·748	5·305	3·30	2·67
Silica	2·271	5·266	0·35	0·75
	100·000	100·000	100·00	100·00

	<i>Amygdalææ.</i>		<i>Papilionaceæ.</i>
	Ash of <i>Cerasus avium</i> .		Sapan wood.
	Engelmann.		Köchlin.
	Wood.	Bark.	
Potash	25·90	7·94	5·02
Soda	10·47	15·48	3·29
Lime	35·78	44·67	77·32
Magnesia	11·47	5·43	2·97
Peroxide of iron....	0·07	0·21	1·36
Phosphoric acid....	9·63	3·47	3·49
Sulphuric acid	4·11	0·86	2·42
Chlorine.....	..	..	3·15
Chloride of sodium..	..	0·66	..
Silica	2·57	21·28	0·39
	100·00	100·00	100·00
Per-centage of ash.....	0·28	10·37	0·85

Liebig's *Annalen*, liv. p. 341–356, 360–363; lvi. p. 122; lvii. p. 67–78.

Contribution to our Knowledge of the Salts of Picric, Nitrophenisic and Chrysolepic Acids. By Dr. T. RIECKHER.

In this treatise the author shows that the picric, nitrophenisic and chrysolepic acids, although the two former have been regarded as identical by Laurent, decidedly differ from one another in their salts.

The chrysolepic acid was prepared accurately according to the directions given by Schunck*, by acting with nitric acid on aloes; the acid obtained treated with carbonate of potash, and separated in a pure state by the addition of muriatic acid.

Chrysolepate of Potash.—The pure acid was neutralized with potash, and the salt obtained by repeated recrystallization in large needles, which exhibited a brilliant play of colours. When the salt

* Liebig's *Annalen*, vol. xxxix. p. 1.

is again dissolved in water, and allowed to crystallize slowly, it is obtained in long, quadrilateral, bright red needles. The oftener the salt is crystallized, the more evident does the bright red colour become, while the reflexion of the blue colour decreases in the same proportion as the bright red increases. The salt is obtained purest from chrysolepate of the protoxide of mercury and chloride of potassium. The chrysolepate of potash explodes with the same violence as the pierate. When concentrated sulphuric acid is poured over it, and it is gently heated, at first water evaporates; but on further heating, the acid is decomposed with evolution of suffocating vapours, and sulphate of potash is left behind. Dried at 392° , and decomposed with sulphuric acid, the salt yielded 17.69 potash; and dried at 266° , 17.47 per cent. potash. The found atomic weight is from the mean of the two, 3356.2; the calculated, 3356.19; the formula is consequently $\text{KO}, \text{C}^{12} \text{H}^2 \text{N}^3 \text{O}^{13}$.

Chrysolepate of Barytes.—This salt may be prepared from the carbonate, muriate or nitrate of barytes. It is tolerably soluble, and crystallizes from the aqueous solution in broad irregular laminæ, and from a dilute spirituous solution in regularly grouped plates, the colour of which is yellow by transmitted light, and dark red by reflected. In large masses, the dark red colour has a velvety appearance. If an aqueous solution be allowed to evaporate spontaneously, the salt is obtained in flattened prisms, sometimes 2 inches in length, on the broad surfaces of which smaller crystals are deposited. Dried between 248° and 392° , the salt lost, I. 14.00, II. 14.00, III. 13.47, IV. 14.24 per cent. water; and on ignition it yielded 22.83 per cent. baryta, and the anhydrous salt 25.60 per cent.; consequently the air-dried salt is $\text{BaO}, \text{C}^{12} \text{H}^2 \text{N}^3 \text{O}^{13} + 5\text{HO}$, which corresponds to 22.32 per cent. baryta and 13.10 water. The atomic weight of the salt is 4285.60, that of the anhydrous salt 3723.20. At 446° acid escapes and the salt becomes imperfectly soluble in water.

Chrysolepate of Strontia.—This salt is obtained in the same manner as the preceding; it is deposited from the dark coloured liquid as a mixture of crystalline laminæ of metallic lustre. It is soluble in water and in tolerably strong spirit. The air-dried salt lost at 266° , 16.85 per cent. water; the anhydrous salt contained 18.61 per cent. strontia; consequently the atomic weight is 3477.7. The formula is $\text{SrO}, \text{Chry} + 6\text{HO}$; at 446° the salt begins to decompose, and then no longer dissolves entirely in water.

Basic Chrysolepate of Lead is obtained, according to Schunck, in bright yellow brilliant metallic laminæ; by mixing a boiling solution of the potash or soda salt with an excess of acetate of lead the author however always obtained it in acicular crystals. When however a mixture of the ammoniacal salt is heated with acetate of lead to boiling, and basic acetate of lead is gradually added until the precipitate no longer dissolves the above laminæ are obtained, but the presence of a basic salt appears to be essentially requisite. The salt gave, I. 47.39, II. 47.42 oxide of lead; Schunck found 47.56, and the formula $3\text{PbO}^2, \text{C}^{12} \text{H}^2 \text{N}^3 \text{O}^{13} + \text{PbO C}^4 \text{H}^3 \text{O}^3$ requires 47.40. When moistened with sulphuric acid, the salt gives

out the odour of acetic acid. When dissolved in water, and acetic acid is added to it, it is decomposed, and on evaporation dark brown metalloid scales of the following salt are obtained.

Chrysolepate and Acetate of Lead.—The crystals dissolve only partially in boiling water, a portion being converted into basic salt. Ammonia produces in a concentrated solution a yellow precipitate, which on warming becomes darker, and appears to be identical with the basic salt obtained by boiling. The air-dried salt lost, between 248° and 266° , I. 5.33, II. 4.85, III. 4.50 per cent. water, and yielded 43.10 per cent. PbO ; the formula $\text{PbOChry} + \text{PbO}\bar{\text{A}} + 3\text{HO}$ requires 5.16 per cent. HO and 42.68 PbO .

Neutral Chrysolepate of Lead.—When the free acid is added to a solution of nitrate of lead, acicular crystals are obtained on slow evaporation, which by reflected light are reddish; by transmitted, yellow. When dried, these needles form a yellowish-red powder. If the salt be dissolved in dilute spirit and allowed to evaporate, delicate yellow needles are obtained. On long-continued boiling with water, an insoluble basic salt separates. It melts at 266° , becomes brown at 446° , and leaves a residue on solution. Between 212° and 266° the air-dried salt ($\text{PbO}, \text{Chry} + 5\text{HO}$) loses 4 equiv. water, and at 392° becomes anhydrous.

Tribasic Chrysolepate of Lead.—When the neutral salt is treated with ammonia, or the ammoniacal salt precipitated with tribasic acetate of lead, a dark yellow amorphous precipitate is obtained, which is represented by the formula $3\text{PbO}, \text{Chry}$.

Pentabasic Chrysolepate of Lead is obtained by treating the last salt with ammonia, and applying heat. It is a dark yellow amorphous powder, containing 70–71 per cent. oxide of lead, and has the formula $5\text{PbO}, \text{Chry}$.

The lead salts detonate with the greater violence the more basic the combination. They explode when warmed with sulphuric acid; with sulphate of ammonia they yield chrysolepate of ammonia and sulphate of lead.

Chrysolepate of Soda was prepared in the same manner as the potash salt, than which it is far more soluble. On evaporation of the solution, a salt separates in crystalline crusts, or in small shining striated needles. The author could not obtain it in long needles, as stated by Schunck. Formula, NaO, Chry .

Chrysolepate of Silver was obtained, by mixing a hot solution of the potash or ammonia salt with neutral nitrate of silver, in small dark red needles on cooling. It yielded 34.25 per cent. silver, and has the formula AgO, Chry . On heating, it explodes with evolution of a shower of sparks.

Chloride of calcium does not decompose the chrysolepate of potash. When sulphate of magnesia is mixed with chrysolepate of soda and evaporated, red needles or plates are obtained; and on further evaporation, a crystalline paste of yellow needles, which owing to their solubility cannot be washed. Perchloride of copper, or nitrate of copper, are not decomposed by chrysolepate of potash.

Hydrated oxide of copper is only dissolved in small quantity by the acid; on slow evaporation and recrystallization, dark red acicular crystals are obtained.

If a solution of chrysolepic acid and ammonia, with an excess of the latter, be allowed to evaporate by exposure to the air, dark elongated octahedrons with rhombic base are obtained, which exhibit a dark blue colour by reflected light, yellowish-brown by transmitted. Their solution is purple-red, with a tint of brown.

Decomposition of Chrysolepic Acid by Sulphuretted Hydrogen.—

When a spirituous solution of chrysolepic acid is saturated with ammonia, sulphuretted hydrogen then passed through, and the liquid evaporated nearly to dryness in the water-bath in order to expel the excess of sulphuret of ammonium, a yellow crystalline substance is obtained on dissolving the residue; and the addition of acetic acid, which is readily soluble in water and spirit, yields an easily soluble compound with potash, and forms with nitrate of silver dark crystals. If the substance moistened with acetic acid be evaporated to dryness, and the residue treated with æther, minute laminæ of a reddish colour are obtained on evaporation. The small quantity of this new substance did not admit of an accurate examination; picric acid however forms no such combination.

The *nitrophenisic acid* was prepared by treating pure hydrate of phenyle with nitric acid, and agreed as well as the potash, barytic and silver salts with what has been published respecting them by Laurent. Laurent mentions three combinations with lead,— $3\text{PbO } 2\text{Ni}$, $2\text{PbO } \text{Ni}$, and $5\text{PbO } \text{Ni}$. If a boiling solution of nitrophenisate of ammonia be mixed with a boiling solution of acetate of lead, there is obtained, according to Laurent, a mixture of two salts, one darkish yellow, and in small crystals, which is first deposited; the other light yellow, which crystallizes in elongated shining lamellæ. By agitation with water and decantation, the latter may be separated, and then forms oblique prisms with rectangular base, and explodes on being struck. The author obtained these two compounds in the above manner, but they could not be separated by solution and recrystallization. It was moreover remarkable that two basic salts should be formed on the employment of neutral compounds; the mother-ley, moreover, which should consequently contain free acetic acid, did not possess a stronger acid reaction than the solution of acetate of lead. The author therefore endeavoured to obtain, instead of the two compounds, only one, and that as pure as possible. If some acetic acid is added to the boiling solution of acetate of lead, the lead salt, consisting of light yellow prisms with rectangular base, is obtained on cooling. On analysis it yielded 42·36–42·29 and 42·75 per cent. oxide of lead. The formula $\text{PbO}, \text{Ni} + \text{PbO}\bar{\text{A}} + 3\text{HO}$ requires 42·68 per cent. oxide of lead and 5·16 water. Laurent obtained 42·8 per cent. oxide of lead and 3·6 water, and thence formed the formula $3\text{PbO } 2\text{Ni} + 3\text{HO}$. The nitrophenisate differs in crystalline form and colour from the chrysolepate $\text{PbO } \text{Chry} + \text{PbO } \bar{\text{A}} + 3\text{HO}$. If acetate of lead be added to nitrophenisate of

lead (obtained by decomposing the ammonia salt with nitrate of lead and crystallization), the above compounds are obtained on evaporation.

If bibasic acetate of lead be precipitated with nitrophenisate of ammonia, an orange-coloured salt is obtained, which dried at 248° yielded 50.08 and 49.98 per cent. oxide of lead. The formula 2PbO Ni requires 50.20 per cent. oxide of lead; the salt is consequently identical with that described by Laurent. The same salt is likewise obtained by adding nitrophenisate of ammonia to sesquibasic acetate of lead. The formation of a bibasic salt under such circumstances is highly characteristic for nitrophenisic acid, and at the same time explains the formation of a basic compound from two neutral salts. When acetate of lead and nitrophenisate of ammonia come together, bibasic nitrophenisate of lead is formed; but since 1 equiv. of the ammonia salt decomposes 2 equiv. acetate of lead and 1 equiv. acetic acid is set free on the formation of the basic compound, the formation of the latter must depend on the eliminated acetic acid. At a certain stage this prevents the formation of the basic salt, and a combination of the neutral salt with acetate of lead separates.

The neutral nitrophenisate of lead, $\text{PbO}, \overline{\text{Ni}}$, is obtained by mixing nitrophenisate of ammonia with nitrate of lead, in concentric groups of minute needles.

The lead salts of *picric acid* form, with the exception of the bibasic, mere amorphous precipitates. If a solution of picrate of ammonia, to which some ammonia has been added, is thrown down with acetate of lead, an amorphous precipitate is obtained, varying in colour from a bright yellow to orange. Dried at 248° , it yielded 70.83 and 71.58 per cent. oxide of lead; the formula 5PbO Pi requires 70.59.

If picrate of ammonia be precipitated with tribasic acetate of lead, a yellow powder is obtained, which dried at 248° gave 60.92 and 60.50 per cent. PbO ; the formula $3\text{PbO } \overline{\text{Pi}}$ requires 60.19. The same compound is obtained by digesting neutral picrate of lead, prepared by precipitating picrate of ammonia with acetate of lead, with excess of ammonia in the cold, while on the application of heat $5\text{PbO}, \overline{\text{Pi}}$ is formed.

If bibasic acetate of lead be precipitated with picrate of ammonia, a bright orange precipitate is obtained, which dried at 302° lost 8.91 per cent. water, and ignited after desiccation gave 51.01 per cent. oxide of lead; the formula $2\text{PbO } \overline{\text{Pi}} + 5\text{HO}$ requires 9.19 per cent. water, and $2\text{PbO } \overline{\text{Pi}}$ contains 50.50 per cent. oxide of lead.

A cold solution of nitrate of lead is not decomposed by picric acid, but on boiling a yellow crystalline precipitate is formed of bibasic picrate of lead.—*Archiv der Pharm.*, xliv. p. 149.

On the Composition of Taurine. By Prof. J. REDTENBACHER.

Demarçay was the first who made an elementary analysis of taurine, which was discovered by L. Gmelin in 1824; he advanced for

it the formula $C^4 NH^7 O^{10}$, which was confirmed by Pelouze and Dumas. Gmelin had observed that taurine dissolved in sulphuric acid without alteration, as well as that nitric acid had no effect on it, which observation the author has also repeated. However, it was highly improbable that a neutral body containing 63 per cent. oxygen should in no way yield products of decomposition which might throw light on its nature. The author therefore conveyed some taurine into potash in a state of fusion, and decomposed the melted and cold mass with dilute sulphuric acid, when a considerable quantity of sulphurous acid was disengaged. The materials employed were pure; the sulphurous acid could therefore only arise from the taurine. On ignition upon platinum foil, the carbonized taurine likewise gave off sulphurous acid, thus placing beyond all doubt the presence of sulphur in taurine.

Nevertheless the quantitative estimation of the sulphur presents great difficulty, for it is so intimately combined in the taurine, that it can be determined neither by nitric acid nor by *aqua regia*, but only by combustion with nitre. Since now, on igniting the taurine in a platinum crucible with nitrate of soda and carbonate of barytes, an excess of sulphur was obtained, and on burning it with nitrate and carbonate of soda a loss resulted, it was ignited in a glass tube. The weighed quantity of taurine was mixed with a powdered quantity of nitrate and carbonate of soda in the mortar, transferred into the tube as in organic analysis, and carefully burnt. The residuary saline mass, together with the pieces of the tube which had cracked on cooling, was boiled with muriatic acid and water, the liquid evaporated to dryness, the silicic acid separated by filtration, and the sulphuric acid precipitated from the filtered solution with a salt of barytes. In this way four experiments gave on an average 25.70 per cent. sulphur.

As however this hitherto unknown amount of sulphur might be the cause of the relations of the other elements of taurine being erroneous, the author submitted it to analysis:—

Redtenbacher. Demarçay. Pel. and Dumas.

Carbon	19.28	19.27	18.90 =	300.0	19.2
Hydrogen	11.25	11.20	11.19	175.0	11.2
Nitrogen	5.73	5.67	5.66	87.5	5.6
Oxygen	38.04			600.0	38.4
Sulphur	25.70			400.0	25.6

Taurine, $C^4 NH^7 O^6 S^2$, is accordingly a substance most rich in sulphur; and as it is a product of decomposition of the bile, this itself must be a sulphurous body, and the ideas respecting the function of the bile be consequently modified. In a body so neutral as taurine, which resists nearly all reagents, it is difficult to decide in what way the sulphur is combined. On treating a solution of taurine with nitrate of silver and ammonia, not the least reaction occurs any more than on boiling with barytic water. If however the sulphur were contained in it in the state of sulphuric acid, a precipitate would certainly result in the barytic water. As already observed, neither nitric nor nitromuriatic acid acts upon taurine, nor even dry

chlorine ; but if it be heated to decomposition in the bulb of a reduction-tube, whilst a current of dry chlorine gas is passed over it, a small quantity of a liquid is obtained, in which sulphuric acid may be detected. If taurine be oxidized with caustic potash, and the residuary saline mass decomposed with dilute sulphuric acid, sulphuretted hydrogen and sulphurous acid are evolved, and sulphur separates precisely as if the potash had been treated with pure sulphur.—Liebig's *Annalen*, lvii. p. 170.

On the Estimation of the Sulphocyanogen in the Saliva.
By SAMUEL WRIGHT, M.D.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,—In the Number of your excellent Journal for May 15th, is an article "On the Presence of Sulphocyanogen in Human Saliva." Its author, Max. Pettenkofer, takes an exception to my process for determining the proportion of sulphocyanogen in this fluid, on the ground that the presence of chlorides would interfere with the results. The passage I allude to runs thus :—"To estimate the sulphocyanogen in saliva, Wright advises us to form sulphocyanide of lead, to weigh this, and to calculate the quantity of sulphocyanide of potassium in the saliva from it; but the metallic chlorides, &c. in the saliva inevitably produce error, consequently, according to Wright's experiments, the amount of sulphocyanogen in the saliva is much too great" (p. 191). How Pettenkofer could have imagined that I should advise the addition of a salt of lead to an *alcoholic* extract of saliva, with the object of determining the presence and proportion of sulphocyanogen, I am quite at a loss to conceive. At least I am assured, in the singular mistake he has committed, that he can either have not read in detail my analytical process, though it has been three several times translated into the language of his country, or have paid only very slight attention to it. In either case he does both himself and me injustice in his reference and the reasoning upon it.

To correct the error into which Pettenkofer has fallen, and free myself of the charge of having committed the blunder in question, I will give, Sir, with your permission, the process I employ in the analysis of healthy saliva. It will be seen that, instead of advising the salt of lead to be added to an *alcoholic* extract of saliva, it is to the *athereal* extract, which, of course, would contain no chlorides.

Filter the saliva through moderately coarse filtering paper. On the filter will remain a solid residuum (1), and a clear liquid (2) will have passed through.

Examination of Solid Residuum (1).—It is to be washed thoroughly on the filter with æther, when a residue (A) will be left, and an æthereal solution (B) will be obtained.

Examination of (A).—Exhaust with cold distilled water; this

dissolves the chlorides of sodium and potassium (*a, b*), which may be obtained by evaporation. The matter left upon the filter is to be dried, weighed, and then incinerated. The amount of loss thus occasioned indicates the proportion of free albumen (*c*). A little ash remains, from which distilled water extracts carbonate of soda (*d*), leaving undissolved phosphate of lime (*e*).

Examination of (B).—Evaporate carefully to dryness, wash the residuum on a filter with distilled water, and continue to treat with this menstruum until everything soluble in it is removed. The aqueous solution is next to be evaporated to dryness, when a residue of pure ptyaline (*f*) will be obtained. The matter left upon the filter is a fatty acid (*g*), which is to be dissolved in æther, from which again, by evaporation, it may be obtained in a pure form.

Examination of Filtered Liquid (2).—This liquid is affected neither by boiling nor by nitric acid; yet it contains albuminate of soda (*h*), which can only be separated by means of galvanism. To this end, it is advisable to reduce the liquid, by very careful evaporation, to one-third in volume, and then to introduce the wires of a galvanic battery in action, free soda will collect upon the negative pole, and coagulated albumen upon the positive one. If this process be conducted carefully, all the albuminate of soda may be removed without decomposing the chlorides.

The liquid, having been thus treated, is next to be very carefully evaporated to dryness, and the dry residuum exhausted with æther, which dissolves the lactates of potash and soda (*i, j*) and the sulphocyanide of potassium (*k*). These salts (after the evaporation of the æther), having been dried and weighed, are to be dissolved in distilled water, and subacetate of lead added until it shall cease to afford a precipitate. An insoluble sulphocyanide of lead will be deposited, and a soluble lactate will remain in solution. The former, after having been dried and weighed, will indicate the proportion of sulphocyanide of potassium previously existing in the saliva; and by subtracting this weight from that of the original saline matter, the quantity of the lactates will also be determined.

The residuum from which these salts have been separated is to be treated with alcohol, which will remove the remaining chlorides of sodium and potassium, the weight of which is to be added to that of (*a, b*).

After the extraction of the chlorides, the soda, which remains in the form of carbonate, is to be neutralized by acetic acid, and the salt dissolved out by alcohol; by evaporating the alcoholic solution to dryness, and exposing the salt to a red heat, the acetic acid will be destroyed and the soda (*l*) left.

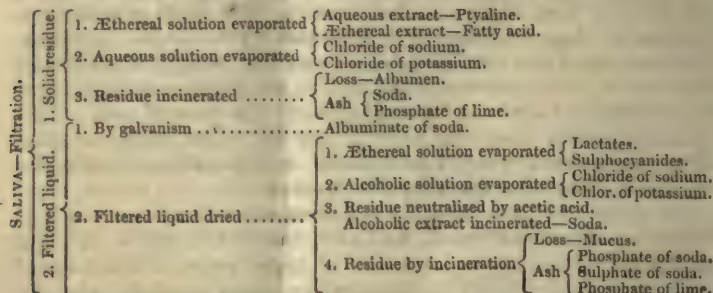
The remaining solid matter is to be dried, weighed and incinerated. The loss by incineration determines the amount of mucus (*m*).

The saline matter left is to be boiled in distilled water, which will generally remove a little sulphate of potash or soda—usually a phosphate of soda (*n*).

The last residuum will be phosphate of lime; its weight must be added to that of (*e*).

Silica is mentioned as a constituent of saliva. I have never met with it, though I have occasionally discovered in it a trace of iron.

The analytical process just described will perhaps be rendered more intelligible by reference to the subjoined diagram:—



As far as my analyses of saliva enable me to judge of this fluid in its healthy state, the following are its ordinary constituents and their proportions:—

Water	988·10
Ptyaline	1·80
Fatty acid	0·50
Chlorides of sodium and potassium	1·40
Albumen, with soda	0·90
Phosphate of lime	0·60
Albuminate of soda	0·80
Lactates of potash and soda	0·70
Sulphocyanide of potassium	0·90
Soda	0·50
Mucus, with ptyaline	2·60

I have no opinion to offer upon Pettenkofer's process for determining the proportion of sulphocyanogen in saliva, further than that, though it may be accurate enough, yet I do not consider it *nearly so simple*, and by no means *more sure*, than the one I ventured five years ago to propose.

I am, Sir,

38 Waterloo Street, Birmingham,
June 1st, 1846.

Your obedient Servant,
SAMUEL WRIGHT, M.D.

On the supposed Property of the Bile of converting Sugar into Fat.
By Dr. J. SHIEL.

In a treatise on the origin of fat in the animal body, Dr. Meckel describes some experiments made under the superintendence of Dr. Marchand, which according to his view completely explain the part which the bile acts in the process of digestion. In the opinion of Dr. Meckel, the bile is destined to transform the sugar, and consequently all articles of food free from nitrogen, into fat. The way in which Dr. Meckel describes his experiments leaves however room

for doubting whether he actually obtained fat. He found by exposing a mixture of 110 grms. bile and 4 grms. grape-sugar for 24 hours to moderate heat, and then treating it with æther, besides some cholesterine, another body which dissolved in potash; this is the whole of his proof for its fatty nature. The doubt as to the correctness of these experiments is increased by the simple consideration that the Carnivora likewise secrete bile, which is not widely different in its composition from ox-bile, and which certainly cannot be destined to transform the sugar which this class of animals devours, or rather does not devour, into fat. The results of some direct experiments which I have made on this subject do likewise not confirm the view taken by Dr. Meckel.

About $\frac{1}{2}$ lb. of fresh ox-gall was shaken with æther as long as anything was removed from it, and then mixed with about an equal weight of a concentrated solution of sugar prepared from starch with diastase; the mixture was kept in a closed vessel for 48 hours in a water-bath at a temperature of 97° , and then divided into two equal portions. One of these was shaken for half an hour with $\frac{1}{2}$ lb. of æther, and the decanted æther evaporated. It left a scarcely appreciable quantity of a greenish body, and which, from the small amount, could not be submitted to further examination. The second portion was retained for 24 hours longer at the above temperature, and then shaken with æther, to which it yielded, besides a trace of cholesterine, a small quantity of a body likewise coloured green by biliary colouring substance, which on solution in potash, precipitation by muriatic acid and solution in alcohol, remained, on evaporation of the latter, as a viscous substance, presenting not the least trace of a crystalline appearance.

Second Experiment.—About $\frac{1}{2}$ lb. of fresh ox-gall was filtered, and divided into two equal portions; one was preserved separate, and the other mixed with a solution of about 70 grms. of grape-sugar prepared from honey, and both exposed in an open flask for 48 hours to a temperature of 94° – 98° , and then extracted with æther. The first portion yielded to this, with the exception of cholesterine, a mere trace of a body soluble in potash, but which on neutralization with an acid merely rendered the liquid opalescent. One-fourth of the æther with which the second portion had been agitated was evaporated; it left scarcely 0.2 gm. of a greenish substance, which contained cholesterine, and yielded to potash a matter which precipitated from the alkaline solution, and dissolved in a little hot alcohol, separated in flakes, and formed on evaporation a yellowish-white viscous substance without any appearance of crystallization, and which melted at 124° – 126° .

It is evident, from these experiments, that bile and sugar, with absence of air, do not act on one another, but that with the access of air the decomposition of the bile is hastened by the presence of the sugar. [The substance obtained can scarcely be anything further than a product of the decomposition of the bile.] I am unable at present to follow out these experiments, much as I regret that the result is a purely negative one.—Liebig's *Annalen*, April 1846.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Method of extracting the Iodine and Bromine contained in the Salts and Mother-liquor of Kelp Soda.

THE Société d'Encouragement, in its general meeting of the 5th June, 1839, decreed a gold medal to Messrs. Delaunay, Couturier and Villedieu, of Tourlaville, near Cherbourg, for their processes for extracting iodine and bromine from soda obtained from the seaweed, which is gathered in large quantities on the shores of Brittany.

The importance of this manufacture was made known in a report inserted in the 'Bulletin' of August, 1839; but it did not contain a description of the process. We will, therefore, make up for this omission, by giving an extract from the patent for ten years, taken by Messrs. Couturier, on the 22nd May, 1835, and which has now become public property.

1st. *Extraction of Iodine from Kelp Soda.*—The mother-waters of this soda having been concentrated to the greatest possible degree, are left in any suitable vessel, in order to allow the salts, which may be separated during its slow crystallization, to deposit; they are afterwards drawn off, and the small quantity of alkaline carbonate, which is always contained in these mother-liquors, is saturated by means of sulphuric acid. In order to be certain that the free alkali of the mother-liquors is saturated, the point of saturation must be slightly exceeded, which is ascertained when, after having sufficiently agitated the mother-liquor to which the sulphuric acid has been added, a strip of litmus paper plunged into it is slightly reddened.

It often happens that the mother-liquors of kelp contain a considerable quantity of hyposulphites which precipitate sulphur, and by the decomposition of which sulphurous acid is disengaged; in this case sulphuric acid is added, by small quantities at a time, until no more sulphur is precipitated. This clarified liquor is put into large vessels, which must not be quite filled, to allow the liquor to be stirred from time to time.

The bottles having been placed upon a table, a current of chlorine gas is directed to the bottom of the liquor they contain. This gas must not be disengaged too rapidly, otherwise a great part of it will be lost by traversing the liquor without being dissolved: attention to this is also necessary, in order to ascertain when to stop. It is important that the liquor should be agitated as often as possible, to enable it to combine with the chlorine gas which accumulates in the empty part of the bottles.

The chlorine gas, which is mixed with these mother-liquors, acts first upon the bases of the iodides, saturates them, and separates or precipitates the iodine; this latter appears at first in the form of a reddish substance, which thickens the liquor, but it soon forms into brown flakes, which fall to the bottom. When the liquor appears

no longer to be coloured red, a small quantity must be poured into a glass, and left for a time to allow the iodine floating therein to settle; after which a few drops of concentrated solution of chlorine are poured into the clarified liquor: the passage of the chlorine must be discontinued as soon as the solution ceases to thicken the mother-liquor, which, on being left in a quiescent state, allows the iodine to settle at the bottom in the form of a thick layer of brilliant brown flakes.

If the iodine is required in large flakes, the supernatant liquor may be decanted off immediately, and washed in a small quantity of cold water; it is then to be put into a retort of glass or porcelain, and sublimed; a long tube of glass, of sufficiently large diameter, being adapted to the neck of the retort. The iodine is volatilized by the heat in the form of violet-coloured vapours, which are first condensed in the neck of the retort, and afterwards in the tube, in the form of small plates or flakes, having a metallic lustre. When the vapours cease to be perceptible, the operation is completed: care must be taken to keep a cloth constantly wetted with cold water upon the whole surface of the tube. In working on a large scale, the products of several operations are united, left to drain, and sublimed as above described.

2nd. *Extraction of the Bromine.*—The mother-liquor having been completely exhausted of iodine, is introduced into a tubular retort until it is half-full; powdered peroxide of manganese and concentrated sulphuric acid of commerce are to be added to it, and an apparatus composed of three recipients, which communicate by means of pipes ground with emery, is adapted to the neck of the retort: the distillation is then proceeded with, care being taken not to let it boil too fast. The bromine which is separated by this operation is volatilized and disengaged in the form of gold-coloured vapours, which are partially condensed in the neck of the first receiver in the form of streaks and drops of a reddish-brown liquid, which run down by degrees into the receiver; but as a considerable quantity of water is volatilized at the same time, it is condensed also, and floats upon the bromine, which occupies the lowest part of the liquor. When the coloured vapours cease to be disengaged from the retort, the fire is removed; a fresh quantity of peroxide of manganese and sulphuric acid are then added, the retort is closed, and the fire again applied. If a sufficient quantity of these substances has been added at first, all the bromine will have been extracted; it then only remains to collect that which is below the liquor condensed in the receiver; this is done by means of a glass-funnel furnished with a cock. When the separation is well-effected, the end of the funnel is placed in a bottle, the cock is gently opened, and the bromine runs into the bottle; the cock is shut the instant all the bromine has run through and the water is about entering. This water holds a considerable quantity of bromine in solution, which is separated from it by collecting the residuum and saturating it with a sufficient quantity of potash. The product of this saturation is afterwards evaporated to dryness, and the residue is calcined at a

dull red heat with a small quantity of coal-dust; it is then dissolved in just a sufficient quantity of water; the solution is filtered and treated in the apparatus with peroxide of manganese and concentrated sulphuric acid, as above described.

The bromine thus obtained is rectified by distillation.—*From the Bulletin de la Société d'Encouragement, as inserted in the London Journal of Arts.*

On the Cleaning of the Wire Cylinder of the Safety-Lamp.
By THEODORE F. MOSS.

The ordinary method of cleaning the wire cylinder of the safety-lamp, by heating it over the flame of burning shavings, is capable of much improvement, as by this process it is found to become brittle, and consequently to impair the safety of using it. The coal dust, which contains more or less sulphur, combines with the oil and forms a tough mass, which hitherto has been taken off by the above way; but the wire becomes red-hot, and readily combines with the sulphur of the coal dust, and consequently becomes brittle and unsafe. In mines where there is much sulphur this is found to be a great inconvenience, and the cylinders must be renewed from time to time, if it is wished that they should retain the quality which their name implies.

In the 'Bulletin du Musée de l'Industrie,' it is proposed to clean the wire cylinders by washing them in a boiling solution of soda, which it effects fully, soap being formed by the combination of the oil and alkali. In Karsten's 'Archives of Mineralogy and Mines,' the cleaning with soda is very strongly recommended, and the experience of several miners given, among which we may relate the following:—

At the Gonley mines, in the district of Worms, the carbonate of soda of commerce is used, which contains 80 per cent. of soda; this, to be rendered caustic, requires an addition of unslaked lime. The soda is dissolved in water, in the proportion of 1 to 10, and 1 part of unslaked lime is added to 4 parts of soda; the whole is then raised to a boiling heat; the wire cylinder to be cleaned is left in the boiling solution about 6 minutes; in this short time the oil has fully combined with the soda, and the soap formed combined with the dirt, after which follows the brushing, rinsing and drying. At the Gonley mine, 40 or 50 of these cylinders are placed at once in the solution, and at the same mines daily from 80 to 90 cylinders washed at the cost per week of 5*d.* to 7½*d.* The same liquid can be used for a length of time by the proper addition of water, soda and lime, especially if the undissolved precipitate is removed, or better if a filtered solution is used.

In the mining district of Saarbruck, soda of commerce contains from 90 to 95 per cent. of soda. The solution is made of 1 part soda to 8 of water; otherwise the same process is followed as at the Gonley mine.

It is to be hoped that, from the simplicity and cheapness of the process, it may be introduced at those mines in this country which may be under the disagreeable necessity of using the safety-lamp.—*Journal of the Franklin Institute*, Feb. 1846.

PATENTS.

Patent granted to John Henry Rehé, for Improvements in the Manufacture of Starch and Farinaceous Food.

THE first part of this invention consists chiefly in extracting, by pressure, from starch, or farinaceous substances largely composed of starch, any water which has been used in grinding, purifying, or preparing the same, whereby the process of drying is accelerated, and any tendency to fermentation is prevented. This may be effected, first, by atmospheric pressure, obtained by exhausting the air from beneath a strainer, on which the mixture of starch or starchy matter is placed; secondly, by forcing air into an air-tight receptacle, which has a strainer fixed at its lower end—the mixture, in this case, is introduced before closing the vessel; thirdly, by forcing the liquid, containing the starch or starchy matter, into a closed vessel, lined with a strainer, and in which vessel numerous perforations are made for the escape of the water; fourthly, by the aid of mechanical pressure, produced by the action of a weight, wedge, wheel, screw, or lever, or hydraulic or other means, applied so as to press upon the surface of the mixture, and drive out the water.

The patentee generally subjects the mixture to atmospheric pressure first, and then to mechanical pressure. The compact mass, thus produced, is subdivided into small angular portions, about three-eighths of an inch in breadth; and these are dried by placing them upon trays, over which a current of air, heated to 120° or 130° Fahr., or even more, is impelled.

The second part of this invention consists in manufacturing starch from unground rice, by exposing it first to a high temperature, and subsequently macerating it in a solution of caustic alkali. 1 cwt. of rice is spread over a surface to the depth of one inch, and exposed to a temperature varying from 160° to 180° Fahr., for two or three hours; after which it is put into a vessel containing water, and agitated for five minutes; the water is then drawn off, and the rice is introduced into a caustic alkaline solution, composed of 4lbs. of pure soda to 70 gallons of water,—potash may be used instead of soda; but the latter is preferred. The rice remains in the solution for five days (being stirred two or three times a day); the liquid is then drawn off, and the rice ground with water to the consistence of cream, and allowed to rest for twenty-four hours; at the expiration of which period the mixture is skimmed, and the clear liquid drawn off by a siphon. 224 gallons of water are now mixed with the rice,

and the mixture is allowed to rest for thirty minutes; by this time the grosser and azotized portions will have subsided, and the upper or fluid part of the mixture, which contains a large quantity of starch, is removed by a siphon into a suitable vessel. The process of adding water, and drawing off through a siphon, is repeated until all the starch is drawn off; and when the starch has subsided in the vessel into which it has been removed, the water is allowed to run off; and it is finished in the usual way, or by the means described under the first improvement.

The third part of this invention consists in manufacturing gum-starch, sometimes called "dextrine" or "amidine," by macerating unground rice in an acidulous solution, at an increased temperature, and afterwards treating it with a caustic alkaline solution. 1 cwt. of unground rice is introduced into a solution, composed of 56 fluid ounces of sulphuric acid, sp. gr. 1.84, and 28 gallons of water,—nitric, hydrochloric, or oxalic acid, may be used instead of sulphuric acid; this solution is maintained at a heat of 135° Fahr., and is kept well-stirred, until the starch, forming part of the rice, is converted into gum-starch, which will be in about three hours; the acid liquor is then drawn off from the macerated rice, and the latter washed by two or three additions of water; after which it is allowed to remain covered with water (being stirred occasionally) for three or four hours, and then the washing is renewed until the greater part of the acid is removed. The rice is now submitted to the caustic alkaline solution, in the manner described under the second improvement.

At the close of the last operation, after drawing off the water, the patentee prefers to give the gum-starch a slight excess of acid: for this purpose, and to prevent any injury to the fabric to which it may be afterwards applied, he employs a vegetable acid (by preference, oxalic acid), adding it in small quantities until an acid reaction is exhibited on the test-paper.—Sealed Oct. 22, 1844.

Patent granted to Benjamin West, St. James's Walk, Clerkenwell, for certain Improvements in covering or stoppering the Tops of Bottles, Jars, Pots, and other similar Vessels.

This invention consists in the application of the electrotype process for depositing metal around, upon and over the upper surfaces of bottles, jars, pots, and other similar vessels, and the corks or other substances used therewith.

The following is the mode of carrying out this invention:—An electrotype apparatus, of a circular form, is constructed, and at or near the bottom of the vessel containing the sulphate of copper or other metal is placed a ring of copper or other metal, which is connected by a wire with the acid; upon the ring are placed, side by side, in an inverted position, the bottles, jars, pots, and other similar vessels, and in a short space of time their tops will become covered with a deposit of metal.—Sealed Oct. 16, 1845.

THE CHEMICAL GAZETTE.

No. LXXXIX.—July 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Contribution to the History of Selenium. By N. W. FISCHER.

ONE of the most remarkable properties of this highly interesting substance is its behaviour during oxidation to form selenic and selenious acid, and likewise in its deoxidation and reduction from these acids. It is this which distinguishes it from sulphur, with which it agrees in so many properties; the two acids of this substance, which are isomorphous with, and in other respects so similar to the acids of selenium, the sulphurous and sulphuric acids, behaving entirely different in respect to their preparation and decomposition. Thus, sulphuric acid can be obtained by acting with nitric acid on sulphur, and still more readily on sulphurous acid, especially with the co-operation of hydrochloric acid. Selenium, on the contrary, is oxidized under these circumstances only to selenious acid. Sulphuric acid boils at 617° , at which temperature it distils over unaltered; selenic acid is decomposed even at 536° into oxygen and selenious acid. Hydrochloric acid, which has no action whatever on sulphuric acid, reduces selenic to selenious acid; in the same way, selenious acid is reduced by sulphurous acid, &c., and by several metals, which have either no action on sulphurous acid; or, when they are oxidized at the expense of a portion of this acid, the other portion enters into combination with the eliminated sulphur, forming hyposulphurous acid, and the result is that a hyposulphite is formed, as for instance is the case with zinc.

The following deviation from these statements, which I recently met with in the preparation of selenious acid, is perhaps worth noticing. I had employed for that purpose nitric acid of 1.5 spec. grav., which at the same time contained a little nitrous acid. The selenious acid, evolved as a beautiful yellow gas, had condensed, precisely as stated by Berzelius, in transparent, shining, long, acicular crystals in the upper part of the retort; but on removing them from the retort and exposing them to the air, they soon became *moist*, and after a time entirely *liquid*. I soon found that the reason of this very remarkable behaviour was the presence of *selenic acid*, as the crystals, when heated with hydrochloric acid, disengaged chlorine, and formed, with a solution of chloride of barium and free hydrochloric acid, a precipitate, which only disappeared on boiling,

and likewise with evolution of chlorine. At first I thought this amount of selenic acid might be explained from the small quantity formed by the concentrated nitric acid (contrary, it is true, to the view hitherto adopted) being carried over in the sublimation of the selenious acid, notwithstanding the high temperature; and I hoped, by redissolving the crystallized acid in water, evaporation, and by quickly and strongly heating the dry residue to decompose the portion of selenic acid, to obtain a sublimate of pure selenious acid. Such however was not the case. After repeated solution and sublimation, the crystals still presented the same behaviour, that is an amount of selenic acid. As the selenium employed contained some sulphur and also a small quantity of copper, I was led to think that the reason of the selenic acid passing over along with the selenious acid undecomposed was attributable to the contemporaneous formation of sulphuric acid, which carried the selenic acid over with it, although it is impossible to explain how the selenic acid remains undecomposed at the temperature at which sulphuric acid distils. I therefore employed pure selenium, which had separated from the solution of the impure in caustic potash by exposure to the air, for the preparation of the selenious acid; but this likewise contained selenic acid, for the large acicular crystals, which on removal from the retort were perfectly dry, soon became moist by exposure to the air, and presented the above-described reaction towards muriatic acid and solution of baryta. I am therefore induced to assume as probable, in order to explain this phenomenon, that selenic acid, combined in a certain proportion with selenious acid, sublimes undecomposed at a far higher temperature than that at which it is decomposed when isolated. The correctness of this supposition, and whether this combination is a peculiar acid analogous to the hypsulphuric acid, or a double acid similar to the combination of sulphuric with sulphurous acid, or of nitric with nitrous acid, can only be decided by further experiments. On this supposition, the crystallized acid obtained under the above-mentioned circumstances would consist, it is true, for the greater part of selenious acid, containing however more or less of the combination of the selenious with the selenic acid, from which indeed it may be readily separated by placing it between filtering paper and pressing it until it remains dry.

The following observation, which I made several years ago and communicated to Prof. Rose, appears likewise to speak in favour of such a combination. When pure selenious acid is dissolved in water, and the solution evaporated between 140° and 212° , or at a still higher temperature, the dry residue appears of a reddish colour, and on re-solution deposits more or less selenium. And this is always the case, however often the acid is dissolved anew, and the filtered solution evaporated to dryness. When this has occurred several times, the dry acid becomes moist, and deliquesces after some time by exposure to the air; in short, the acid contains selenic acid, which has been formed at the expense of a portion of the selenious acid, and consequently with the separation of selenium. Now since

this altered selenious acid is still perfectly dry at a temperature of 68° to 86° , and deliquesces only at the ordinary temperature, it is very probable that it is not merely a mixture, but a chemical combination of the two acids.

Sulphuric acid likewise forms with the selenious acid a similar combination, as is evident from the following:—On acting with concentrated nitric acid upon selenium containing sulphur in the preparation of selenious acid, and strongly heating the white mass obtained on evaporation of the liquid in order to sublime the selenious acid, an oily fluid ran down from the summit of the retort to the bottom in stripes, which, after all the selenious acid had been sublimated, solidified, on the cooling of the retort, to a white amorphous mass, and exposed to the air quickly deliquesced, and reacted like a combination of sulphuric and selenious acid.

Far more remarkable than this behaviour during oxidation is that exhibited in the reduction of this substance from selenious acid. According to my observations, published in 1827, it is not only reduced by zinc and iron, as already stated by Berzelius, but by all metals which reduce silver, and even by this metal*; but the reason of this reduction cannot possibly be identical with that on which the restoration of metals from their solutions by other metals depends, viz. that the latter are more oxidizable or more positively electrical than that in solution, since between selenium and the above-mentioned metals the very opposite obtains; but the reduction of the selenium from the selenious acid depends on the double affinity which the metals have on the one hand to the selenium, and on the other hand in the oxidized state to the selenious acid. Consequently two products are formed in this case, a seleniuret and a selenite, which also stand in a certain proportion to one another, the whole of the selenious acid never being reduced. Accordingly those metals act most powerfully, and even on a very dilute solution of selenious acid, which have a strong affinity for selenium, as is the case with silver, and, according to recent experiments, in a still higher degree with copper. Lead, bismuth and antimony, act far more slowly and less powerfully. If selenium were alone eliminated by zinc and iron, we should have to admit that with these metals merely the elective affinity of the oxides to the acid was active, according to which they become oxidized at the expense of a portion; but Berzelius has found in the selenium reduced by iron some seleniuret of iron, and this may probably be the case likewise with that obtained by means of zinc. The presence of another acid favours the reduction, partly from its dissolving the insoluble selenite which is formed, and partly because it possesses a stronger affinity to the produced oxide than the selenious acid, and consequently combines with it. In this last case, the *whole* of the selenious acid can be reduced. That this favourable effect will depend both on the nature of the foreign acid and of the reducing metal is self-evident.

* This is perhaps the reason why Berzelius still enumerates the selenium as an idioelectrical substance with the metals.

The action which these metals exert on the green solution of the selenium in sulphuric acid is highly remarkable, as they become almost immediately coated with the seleniuret which is formed; this is especially the case with silver and copper. A copper wire placed in the solution very soon forms a crust of seleniuret of copper and selenite of copper, so thick that it can be drawn off in the form of a tube from the undissolved copper wire; likewise those metals which do not reduce the selenious acid, such as gold, platinum and palladium*, exhibit a strong affinity to selenium. When a drop of the green solution of selenium in sulphuric acid is placed on one of these metals and exposed to the air, the selenium gradually eliminated by the absorption of moisture from the air, adheres so firmly to these metals that it cannot be rubbed off.—Poggendorff's *Annalen*, lxxvii. p. 411.

On the Volatile Oils of several Cruciferous Plants. By F. PLESS.

The investigations of Wertheim†, on the connexion existing between oil of garlic and oil of mustard (sulphuret of allyle and sulphocyanuret of allyle), and the well-known fact that most of the *Cruciferae* are characterized by acrid volatile substances, led me to suppose that there might be a plant in which these two compounds of allyle might coexist. During last autumn and the present summer I have examined the volatile oils of several of our *Cruciferae*, and found at least four distinct bodies in them. As however the quantity of substance obtained was very small, it was impossible to submit them to a more perfect examination. I found however the idea with which I started confirmed.

Oil of Thlaspi arvense.—When the herb or seed of this plant is pounded, mixed with cold water and distilled, after a time a colourless oil is obtained of a peculiar penetrating odour and burning leek-like taste, at the same time calling to mind the oil of garlic and that of mustard. On saturating it with ammonia, subsequently adding water and distilling, the inspissated residue yields beautiful crystals, which prove, from their form, solubility in water and alcohol, bitter taste, meltingpoint at 161° , their mode of decomposition by heat, and their precipitates with solutions of mercury, silver and platinum, to be thiocinnamine.

On combining the excess of ammonia contained in the distillate with sulphuric acid, the odour of the pure sulphuret of allyle is perceptible, and on redistillation it is obtained pure and colourless. The alcoholic solution of the oil yielded with chloride of platinum an orange precipitate, which gave on analysis $C^{24} H^{20} Pt^1 Cl^3 S^9$. This is the double salt of platinum ($PtCl^2, C^6 H^5 Cl$) + $3(PtS^2, C^6 H^5 S)$ described by Wertheim‡.

It is thence evident that the volatile oil contained in *Thlaspi ar-*

* Palladium has a slight reducing action on selenious acid at a high temperature.

† Chem. Gaz., vol. iii. p. 495.

‡ Chem. Gaz., vol. iii. p. 180.

vense is a mixture of oil of garlic and mustard. Neither of the bodies is contained as such in the seed any more than oil of mustard in *Sinapis nigra*. The powdered seed has not the least odour of either of the two bodies; and when heated to 212° or treated with alcohol, yields no oil on being mixed with water. The alcoholic extract leaves on evaporation a crystalline residue mixed with mucilage, which produces, when triturated with water and the seeds of *Sinapis alba* or *S. arvensis*, oil of mustard, but no oil of garlic.

Wertheim has already proved the presence of oil of mustard in the root and herb of *Alliaria officinalis*, and rendered that of the oil of garlic probable; a larger quantity of the two oils is obtained from the seed of this plant by distillation after the action of water. The oil of mustard may readily be freed from that of garlic by the addition of a small quantity of platinum and some alcohol, facilitating the formation of the precipitate by agitation, and then distilling with water. 0.287 grm. of the precipitate left on ignition 0.139 grm. of platinum or 48.4 per cent.

If an excess of chloride of platinum be added, the oil of mustard likewise disappears after some days, and the yellow precipitate then contains a few per cent. more platinum than correspond to the double compound of the oil of garlic.

The mixture of the two oils amounted in my experiments to about $\frac{3}{5}$ per cent. of the seed, of which 9 out of 10 parts consisted of oil of mustard, while this formed only about one-tenth in the mixture of the oil from *Thlaspi arvense*. This relation however of the two oils is not constant in the plants: I found specimens of *Alliaria officinalis* from a more sunny locality not to contain a trace of garlic oil.

Oil of mustard without garlic oil is also contained in the herb and seed of *Iberis amara*, and likewise in very small quantity in the seed of *Capsella Bursa pastoris*, *Raphanus Raphanistrum*, and *Sisymbrium officinale*.

Oil of Lepidium rudemale.—When this common plant is crushed, mixed with water and distilled, after a short time a milky liquid is obtained, which on being rectified once or twice yields a peculiar yellow oil. The rectification must not be carried on in copper vessels, but in glass retorts, because in the former a portion of the oil is decomposed; nor should the distillation be delayed; for once, when I had macerated the crushed herb for 10 hours with water, not a trace of oil could be found. The oil is heavier than water, has the peculiar refreshing, but at the same time somewhat leek-like odour, and the warm taste of the water-cress. Its vapours produce, when inspired in large quantity, a disagreeable sensation of dryness in the larynx, and headache. After repeated rectification with water, it is obtained colourless; it soon however becomes yellow again on exposure to the light. Without water it can neither be rectified in the oil-bath nor over the naked fire without decomposition. It is very sparingly soluble in water, but readily soluble in alcohol and æther; the solutions have no action on litmus-paper. It dissolves in concentrated sulphuric acid with a red colour, and is again sepa-

rated on the careful addition of water. Solution of potash and ammonia occasions no perceptible reaction.

Chloride of platinum produces after some time in the alcoholic solution a beautiful deep yellow, and perchloride of mercury a white precipitate. With nitrate of silver I once obtained a white and once a black precipitate; the latter was sulphuret of silver. Proto-nitrate of mercury immediately produces a precipitate of sulphuret of mercury. When the oil is oxidized with nitric acid, solution of barytes yields a precipitate insoluble in acid; the oil therefore contains sulphur.

The oil does not pre-exist in the seed of the plant, but is produced by the action of water, for the powdered seed has no smell, and no longer yields any oil after being exposed to a tolerable heat, or after treatment with alcohol.

The seeds of *Lepidium sativum* and *L. campestre* exhibit the same properties. After the action of water they yield an oil in every respect similar to the above.

Oil of Raphanus sativus.—The root and seed of this plant yield, on distillation with water, a turbid liquid, which on rectification gives a small quantity of a colourless oil. It has the taste, but no longer the characteristic odour of the radish; is heavier than water, in which it is tolerably soluble. It affords with chloride of platinum a yellow, and with perchloride of mercury a white precipitate. After oxidation with nitric acid, it yields with chloride of barium a precipitate insoluble in water and acids, and consequently contains sulphur.

The seeds of *Brassica napus*, *Cochlearia draba* and *Cheiranthus annuus*, yield an oil having similar properties. It is however only produced after the action of water; heat and alcohol prevent its formation.—Liebig's *Annalen*, April 1846.

On the Salts of Sulphurous Acid. By Dr. C. RAMMELSBERG.

The investigations of the author were made in part after those of Dr. Muspratt, with which they do not altogether agree, although the varying results were tested more than once.

Sulphite of Potash.—The neutral salt was not examined more closely from its crystallizing with great difficulty; a hot saturated solution deposits nothing on cooling; on the contrary, the solution becomes turbid on the application of heat, and clear again on cooling. Muspratt obtained the salt in crystals, with 2 equivs. of water.

Bisulphite of Potash is obtained when sulphurous acid is passed through a warm solution of carbonate of potash until it is in excess. On cooling, or on the addition of alcohol, it is precipitated in a crystalline form. The salt gradually loses a portion of its acid by exposure to the air, and by long boiling it likewise becomes gradually converted into neutral sulphate. In the analysis the potash was determined by evaporation with sulphuric acid, and the sulphurous acid by fusion with nitre and carbonate of soda;—

Potash	39.24	1	39.20
Sulphurous acid	52.60	2	53.32
Water	..	1	7.84

Sulphite of Soda.—The neutral salt is readily obtained by adding to a warm solution of soda saturated with sulphurous acid as much carbonate of soda as had previously been employed; it crystallizes extremely well on cooling, but the crystals become dull and opake on exposure in the air from loss of water. They probably belong to the hemiprismatic system. They are readily soluble in water; the solution becomes turbid on boiling, but clears again on cooling. They dissolve but sparingly in alcohol. At 302° F. they lose the whole of their water, become white and opake, but fuse only at a higher temperature, without any further loss, to a yellowish-red mass, from which alcohol removes 1 equiv. sulphuret of sodium for 3 equivs. sulphate of soda. The analyses of two samples, prepared at different times, yielded—

Soda	24.67	23.50	1	24.75
Sulphurous acid ..	26.20	27.40	1	25.40
Water	..	..	7	49.85

It is consequently $\text{NaO}, \text{SO}^2 + 7\text{HO}$. Muspratt obtained it with 10 equivs. water.

Bisulphite of Soda, formed in the above-mentioned way, crystallizes from the hot acid solution in shining prisms. It smells of sulphurous acid, has an acid reaction, soon effloresces in the air, and is converted into sulphate. It yielded on analysis—

Soda	31.82	2	31.29
Sulphurous acid	63.25	4	65.21
Water	..	1	4.50

Formula, $2(\text{NaO}, 2\text{SO}^2)\text{HO}$. Muspratt obtained crystals with twice the amount of water.

Sulphite of Baryta.—This well-known salt yields, when heated with the exclusion of air, a mere trace of sulphur and water; the yellowish residue obtained after ignition contains not a trace of sulphurous acid, but only sulphate of barytes and sulphuret of barium. That Muspratt obtained sulphur and sulphurous acid was probably owing to his having heated it with access of air. The author obtained on analysis 69.37 per cent. BaO ; the salt is therefore anhydrous.

Sulphite of Strontia.—The precipitate formed in a solution of chloride of strontium by sulphurous acid yielded, after drying in the water-bath, 60.85 per cent. strontia. It is therefore SrO, SO^2 , which contains, according to calculation, 61.74 strontia and 38.26 per cent. SO^2 . The salt forms microscopic, thin, rectangular, four-sided prisms with bihedral summits.

Sulphite of Lime.—The carbonic acid is completely expelled from carbonate of lime by sulphurous acid, and there is left a crystalline powder of sulphite of lime, which contains 35.82 lime, 41.02 per cent. SO^2 , and 23.00 HO ; the formula is consequently

CaO , $\text{SO}^2 + 2\text{HO}$. Gently heated with exclusion of the air and then ignited, the salt yields no volatile products, but a mixture of sulphuret of calcium and sulphate of lime. On evaporating under the air-pump, the solution of sulphite of lime in water saturated with sulphurous acid, a salt is obtained in very minute crystals, which contains much less water than the preceding; it gave 42.77 CaO , and lost 7.00 per cent. water; its formula is therefore $2(\text{CaO}, \text{SO}^2) + \text{HO}$, which requires 43.48 CaO , 49.75 SO^2 , and 6.95 HO . Muspratt found 23.09 per cent. = 2 equivs. water, as in the preceding salt.

Sulphite of Magnesia.—When sulphurous acid is passed into water holding carbonate of magnesia in suspension, a colourless solution is obtained, from which the salt readily crystallizes on evaporation. The crystals are transparent, shining and soluble in about 20 parts cold water; on exposure to the air, they pass into sulphate of magnesia, which is likewise the case on long ebullition with water, without however any sulphurous acid escaping; the flocculent precipitate which forms at the same time is sulphite of magnesia, apparently in the anhydrous state. Heated beyond 212° , the above crystals lose a portion of their water of crystallization, which is entirely expelled only at 392° , when sulphurous acid is disengaged. On ignition, with exclusion of the air, a sublimate of sulphur is obtained; the salt swells, becomes yellow, then brown, and cakes together on cooling to a white residue, which consists of sulphate and pure magnesia, but no sulphuret of magnesium. On analysis, the salt was converted with sulphuric acid into neutral sulphate. Five experiments yielded as a mean 19.14 MgO ; according to the formula $\text{MgO SO}^2 + 6\text{HO}$, the salt contains 19.36 MgO , 30.06 SO^2 , and 50.58 per cent. HO . Muspratt found $\text{MgO SO}^2 + 3\text{HO}$.

Sulphite of potash and sulphite of magnesia yielded apparently a double salt, but the crystals could not be obtained perfectly pure from sulphite of magnesia. The magnesia salt gave no double compound with soda. When a solution of magnesia in sulphurous acid was mixed with an excess of ammonia and the precipitate redissolved by sulphurous acid, only sulphite of magnesia separated at first, but subsequently a double salt crystallized, which was composed according to the formula $3\text{NH}^3, \text{SO}^2 + 3(\text{MgO}, \text{SO}^2) + 16\text{HO}$, or $\text{NH}^4 \text{O}, \text{SO}^2 + 3(\text{MgO}, \text{SO}^2 + 5\text{HO})$.

Sulphite of Zinc.—If oxide of zinc be suspended in water and sulphurous acid passed through it, either the whole dissolves, or a portion of the salt subsides as a crystalline powder. The minute crystals of this sparingly-soluble salt are converted in the air into sulphate; on ignition in a closed vessel, they give off water and sulphurous acid, but no sulphur, and leave a yellowish-white residue, which dissolves in dilute acids with evolution of sulphuretted hydrogen, and contains a large quantity of sulphuric acid. In the analysis, the sulphurous acid was converted by nitre and carbonate of soda into sulphuric acid, and the zinc determined both as sulphate and as oxide. It yielded—

Oxide of zinc ..	42.51	41.36	42.55	42.71	43.31	2	45.61*
Sulphurous acid	33.23	..	..	..	34.34	2	33.74
Water	..	..	..	..	..	5	23.65

According to Fordos and Gélis, the salt contains only 2 eqivs. HO; but they determined the oxide of zinc by igniting the salt, which is not accurate, as the residue always contains sulphuret of zinc and sulphate. Muspratt likewise found only 2 eqivs., although he determined the oxide of zinc from the precipitate produced by carbonate of soda.

Sulphite of Zinc and Ammonia.—This compound is obtained when sulphite of zinc is dissolved in a warm solution of caustic ammonia and somewhat evaporated. On cooling, the salt separates in crystalline crusts; it smells of ammonia, and is decomposed by water, sulphite of ammonia free from zinc being retained in solution. When heated in a glass tube, it disengages water and ammonia, and yields a sublimate of sulphite of ammonia. The salt was boiled with caustic potash, the disengaged ammoniacal vapour passed into muriatic acid, and weighed as chloride of ammonium; the liquid was then supersaturated with muriatic acid, and the zinc precipitated with carbonate of soda. The analysis yielded—

Ammonia	10.33	1	10.57
Oxide of zinc	50.70	2	49.91
Sulphurous acid	..	2	39.52

Sulphite of Cadmium.—When sulphurous acid is passed into water containing carbonate of cadmium in suspension, a perfect solution is obtained, from which the salt is deposited on evaporation in a crystalline form. It is oxidized very slowly by exposure to the air, dissolves sparingly in water, but readily in dilute acids; on ignition, it evolves sulphurous acid, and leaves a yellowish residue of oxide, sulphuret and sulphate of cadmium. In its analysis, the oxide of cadmium was determined as sulphate; it yielded 66.25 per cent. CdO; the formula CdO, SO^2 requires 66.51 CdO, and 33.49 per cent. SO^2 .

Sulphite of Cadmium and Ammonia.—It is obtained in the same way as the zinc compound, and possesses similar properties. It yielded on analysis 7.97 NH^3 and 61.26 per cent. CdO; the formula $2(\text{CdO}, \text{SO}^2) + \text{NH}^3$ requires 8.21 NH^3 , 60.05 CdO, and 30.74 SO^2 .

Protosulphite of Manganese.—This salt gradually separates on mixing protacetate of manganese and sulphite of soda; it is however obtained best from the protocarbonate of manganese and sulphurous acid. It is reddish-white, crystalline, yields when heated in a retort water and sulphurous acid, becoming of a darker colour, and leaves on ignition a greenish-brown residue of sulphuret of manganese, sesquioxide and protosulphate. The manganese was precipitated from the muriatic solution by carbonate of soda and ignited. It gave 38.87–38.85 per cent. protoxide. The formula $2(\text{MnO}, \text{SO}^2) + 5\text{HO}$ requires 39.52 MnO, 35.56 SO^2 , and 24.92 per cent. HO. According to Muspratt, the salt is $\text{MnO}, \text{SO}^2 + 2\text{HO}$.

* Zn = 406.59, according to A. Erdmann.

Sulphite of Nickel.—When recently-precipitated hydrated oxide of nickel is suspended in water and treated with sulphurous acid, a green solution is obtained, which on evaporation in the water-bath deposits an indistinctly-crystalline green mass. This is insoluble in cold and hot water, but soluble in water containing sulphurous acid. When heated with water, the previously transparent salt becomes opaque, undoubtedly from loss of water. When the salt is heated in a retort, it melts, parting with water, again becomes solid and darker, gives off sulphurous acid, and leaves a grayish-green residue (47 per cent.) of sulphate, oxide, and much sulphuret of nickel. In the analysis, the oxide of nickel was precipitated by potash; it yielded 30·60 per cent. NiO, corresponding to the formula $\text{NiO SO}^2 + 6\text{HO}$. Muspratt examined a salt, $\text{NiO SO}^2 + 4\text{HO}$, which had been prepared in the above manner, and separated as a crystalline powder.

If sulphite of potash or soda be added to a solution of sulphate of nickel, a mucilaginous green precipitate is formed, whilst the liquid passes green through the filter, and becomes turbid, with disengagement of sulphurous acid. The residue on the filter soon turns yellow, and then black, and passes gradually into sulphate of nickel.

Sulphite of Nickel and Ammonia.—When sulphite of nickel is dissolved in caustic ammonia and alcohol added, a light blue crystalline precipitate is formed, which dissolves in a little water with a light blue colour, but on the addition of more water, or the application of heat, is rendered turbid. On ignition, this compound gives off water, ammonia, and a sublimate of sulphite of ammonia, whilst the residue presents the same characters as the neutral salt.

The analysis gave—

Ammonia	23·13	$1\frac{1}{2}$	21·04
Oxide of nickel	30·14	1	30·69
Sulphurous acid	..	1	26·22
Water	..	3	22·05

The formula would be $\text{NiO SO}^2 + 1\frac{1}{2}\text{NH}^3 + 3\text{HO}$, like the neutral salt, in which 3HO is replaced by $1\frac{1}{2}\text{NH}^3$.

Sulphite of Cobalt.—Hydrated oxide of cobalt suspended in water dissolves readily in sulphurous acid, and after warming, crystals separate, which, according to Muspratt, are $\text{CoO SO}^2 + 5\text{HO}$. On evaporation of this solution, a large quantity of sulphurous acid is given off, while the salt becomes for the greater part oxidized; the author therefore evaporated the red solution in a retort, while a constant current of hydrogen gas carried off the aqueous vapour and prevented the access of air. A beautiful peach-blossom coloured salt was deposited, under disengagement of sulphurous acid, in minute crystals, which were nearly insoluble in water. On analysis it yielded 37·63 CoO and 32·58 per cent. SO^2 ; the formula $\text{CoO SO}^2 + 3\text{HO}$ requires 38·84 CoO, 33·22 SO^2 , and 27·94 HO. When no more of the salt separates on further evaporation in the retort, and the contents on cooling no longer smell of sulphurous acid, this appears anew immediately on heating it again, and at the same time a light rose-coloured powder subsides, which turns brown on the filter, and

is probably a basic salt. It becomes crystalline and of a darker colour by standing in the liquid.

When ammonia is poured over $\text{CoO SO}^2 + 3\text{HO}$, it becomes blue, and dissolves, with the exception of a green residue, to a reddish-brown solution, which quickly increases in intensity. Alcohol throws down from this a yellow crystalline powder, which contains sulphurous acid and ammonia, and is coloured brown by potash; it therefore contains as base CoO^2 . Its solution in cold muriatic acid yields with ammonia a bright yellow liquid, from which this compound is again deposited in crystalline granules. If to a neutral salt of cobalt sulphite of soda is added, a red precipitate is formed, while the liquid highly coloured by the sulphite is not precipitated before it is concentrated by evaporation; even then it still remains red, and liberates, on the application of heat, sulphurous acid. The precipitate consequently appears to be a basic compound.

Behaviour of Sulphurous Acid towards Oxide of Copper.—When recently-precipitated hydrated oxide of copper is treated with water and sulphurous acid, it dissolves to a bluish-green liquid, from which, on standing or the application of heat, a cinabar-red powder is deposited. The same compound is obtained on bringing together sulphite of potash and salts of the oxide of copper on the application of heat. Hitherto the salt has been considered, according to Chevreul's notion, as the protosulphite of copper ($\text{CuO, SO}^2 + 2\text{HO}$), the formation of which took place simultaneously with that of the sulphate of copper. Muspratt assigns to it the formula $\text{CuO, SO}^2 + \text{HO}$; but the author found it to be a double salt of protosulphite and persulphite of copper. It dissolves in hydrochloric acid with a brown colour, which on dilution turns green. With a small quantity of acid, protochloride of copper separates. The solution yields with potash a brownish-yellow precipitate; with ammonia it becomes of a bright blue colour. This compound appears under the microscope in the form of yellow transparent prisms; when heated in a closed vessel to 302°F. , only traces of interstitial water are given off; at a higher temperature it is decomposed, water and sulphurous acid are liberated, and after ignition a reddish-brown residue remains, which contains, besides protoxide of copper, some persulphate. On heating the salt to redness in a current of hydrogen, water and sulphurous acid escape, and the residue consists of metallic copper with some sulphuret and sulphates. That the salt contains peroxide of copper is also shown, from its muriatic solution, on being boiled with metallic copper without access of air, dissolving a considerable quantity of the metal; the liquid then acquires a light yellow colour, which disappears on dilution, and does not turn green. To determine the quantity of the oxide of copper, the process described by Fuchs for the estimation of the peroxide of iron, was followed; however, it is requisite to boil for a considerable time, and somewhat less copper dissolves than should be the case according to calculation, although with iron the result generally falls out too high, of which the author convinced himself by several experiments. Another circumstance, which has some influence on the analysis,

consists in the formation of some sulphuret of copper; however, the quantity is too small to produce any important error. The sulphurous acid was determined as usual by fusion with carbonate of soda and nitre. The analysis yielded as the mean, 37.11 protoxide of copper, 19.21 peroxide of copper, and 34.88 per cent. sulphurous acid. These numbers, although they cannot be perfectly accurate, prove that the compound must be CuO , $\text{SO}^2 + \text{Cu}^2 \text{O}$, $\text{SO}^2 + 2\text{HO}$, which requires 36.92 $\text{Cu}^2 \text{O}$, 20.53 CuO , 33.23 SO^2 , and 9.32 HO . 36.92 per cent. CuO^2 and 20.53 CuO contain 49.16 Cu ; in the above reduction with hydrogen gas, 49.09 Cu were obtained. When the solution of hydrated oxide of copper in sulphurous acid is mixed with strong alcohol, a brown amorphous precipitate results, which cannot be obtained perfectly pure, but is otherwise identical with the preceding salt. The difference in colour can only be ascribed to an amorphous state.

Double Salts of the Protosulphite of Copper with the Sulphites of the Alkalies.—When a solution of oxide of copper is mixed with sulphite of potash or soda in the cold, yellowish-brown precipitates are formed, which on boiling with water leave the red double salt, which probably pre-existed in them. Under the microscope these precipitates do not appear homogeneous, from the admixture of the red double salt; it is also decomposed very readily. A more stable compound is obtained when such a precipitate is digested while still moist with a concentrated solution of the alkaline sulphite. It dissolves in it to a colourless liquid, which with a sufficient quantity of alkali present can even be boiled. The solution was mixed with alcohol, which separated a very concentrated heavy liquid, from which a salt separated in indistinct crystals *in vacuo* over sulphuric acid. They soon however become coated with a green layer of sulphate of copper when exposed to the air. When preserved for some months in a closed vessel, they had become black, and at some places sulphite of soda had separated. When recent, they are colourless, and dissolve in water, with the elimination of only a few green flakes. The protoxide of copper was determined in the analysis as sulphuret, and the potash as sulphate. It gave—

Protoxide of copper	8.18	1	8.09
Potash	42.22	8	42.82
Sulphurous acid	..	9	32.76
Water	..	16	16.33

The salt will be $\text{Cu}^2 \text{O}$, $\text{SO}^2 + 8(\text{KO}, \text{SO}^2) + 16\text{HO}$, if it contain no uncombined salt of potash. The sulphite of copper appears, on the preparation of this compound, to remain behind in the mother-ley.

Persulphite of Iron.—The persalts of iron are coloured blood-red by an alkaline sulphite. If the whole be heated, sulphurous acid is given off, and a brown body subsides, which according to Kœhne is $\text{Fe}^2 \text{O}^3$, $\text{SO}^2 + 7\text{HO}$. Protoxide of iron remains in solution.

Behaviour of Sulphurous Acid to Peroxide of Mercury.—The author added some water to recently-precipitated well-washed hydrated oxide of mercury, and passed sulphurous acid into it. The

liquid filtered from the powder, which had become white, contained protoxide of mercury and sulphuric acid. The white salt became yellowish on edulcoration. It dissolves readily in warm nitric acid, liberating nitrous acid; forms with hydrochloric acid protochloride of mercury, with disengagement of sulphurous acid; and yields with potash protoxide of mercury and sulphite of potash. On drying, the salt turns yellowish-brown, smells of sulphurous acid, and is quickly oxidized into sulphate, metallic mercury being separated. It is soon decomposed when boiled with water, sulphuric acid and metallic mercury being formed. As the salt cannot be dried well, it was digested moist with solution of caustic potash, and the eliminated protoxide reduced with hydrochloric acid and protochloride of tin. The alkaline liquid was evaporated, and oxidized with nitric acid. In analysis I., which had been prepared at a different time, the mercury was determined as sulphuret, and the small quantity of protoxide dissolved in the potash neglected:—

	I.		II.	
Protoxide of mercury.....	81.36	2	81.21	82.93
Sulphurous acid.....	18.64	3	18.79	17.14
				17.06

A. Vogel found the white powder into which the oxide is converted to consist for the greater part of basic protosulphate of mercury; but in his experiments an excess of acid had undoubtedly been employed, as the peroxide of mercury was conveyed directly into a moderately-concentrated solution of it.—Poggendorff's *Annalen*, lxxvii. p. 245 and p. 391.

Analysis of the Milk of the Cow Tree. By M. HEINTZ.

An analysis of this vegetable milk afforded the following result:—Water, 57.3; vegetable albumen, 0.4; a species of wax (having the formula $C^{35}H^{66}O^8$), 5.8; a resin soluble in cold or boiling alcohol (corresponding to the formula $C^{35}H^{58}O^9$), 31.4; gum and a kind of sugar, 4.7; bases resisting the action of heat, such as magnesia, soda, traces of potash and lime combined with phosphoric acid, and an organic acid undetermined, 0.4 = 100. This agrees nearly with the analyses of MM. Boussingault and Mariano; but differs so much from that by M. Marchand, that M. Heintz suspects he may have examined the milk of another species of plant.—Silliman's *Journal*, May 1846.

CHEMICAL PREPARATIONS.

On a new Process for obtaining pure Chlorine Gas.

By Profs. R. E. ROGERS and W. B. ROGERS.

THIS process is founded on the powerful oxidating action of chromic acid, especially when liberated in a solution, and consists in causing a reaction between hydrochloric acid and this substance, in

which the chlorine of the former is set free. Our mode of proceeding is as follows:—

To 1 part of powdered bichromate of potash, in a small retort or flask, we add 6 parts of hydrochloric acid, of spec. grav. about 1.16, and apply a gentle lamp heat for a few seconds, so as to bring about a brisk reaction. The chlorine is now rapidly evolved, and continues to be disengaged as fast as is convenient, without requiring any further application of the lamp.

Referring to the composition of the bichromate of potash and of hydrochloric acid, it will be seen that 1 *equivalent of bichromate of potash and 7 of hydrochloric acid, are capable of evolving 3 equivs. of chlorine*, at the same time giving rise to 1 equiv. of the sesquichloride of chromium, 1 of the chloride of potassium, and 7 of water.

In order to ascertain how near we might approach to the equivalent quantity of chlorine above deduced, we resorted to the following method:—Knowing that a strong solution of chloride of sodium is much less absorbent of the gas than ordinary water, we prepared a quantity of saturated brine, through which we passed chlorine until the liquid appeared to be fully charged. With this we filled a tall graduated vessel, designed to receive the gas, and a porcelain bowl, which served as a pneumatic trough, and having placed 4 grms. of the bichromate with an excess of hydrochloric acid in a small retort, we passed the gas as it was evolved through the chlorous saline solution into the narrow graduated jar. After urging the process until the action entirely ceased and no further gas escaped, we measured the resulting gas with the usual precautions at 60°. Its volume was found to be 54.5 cubic inches. On repeating the experiment with the same amount of bichromate and acid, and with the same brine, we obtained in the second trial 55.5 cubic inches, and in the third 56.2 cubic inches of the gas, the increase being evidently due to the diminished absorption arising from the more complete saturation of the liquid with chlorine.

Taking 76.5 grs. as the weight of 100 cubic inches of chlorine at 60° F., the volume due to the entire decomposition of 4 grms. of bichromate of potash is 57.3 cubic inches. It thus appears that, with proper precaution, this process may be made to yield $\frac{56}{57}$ ths, or nearly the whole theoretical amount of the gas.—Silliman's *Journal*, May 1846.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Steel. By Dr. CARL SCHAFHAEUTL.

IRON, in the composition of which a portion of the silica is replaced by manganese, will, while being smelted, rather part with the latter than the former. From this it follows, that at the moment when

the iron is on the point of passing from a liquid to a solid state it will retain sufficient silica to form steel. For this reason, during the whole process of refining, the current of air is caused to act rather upon the surface of the metal than through the interior of the fluid mass, in order to avoid the combustion of too much carbon and silica; from which it follows that the casting becomes malleable without losing a sufficient quantity of silica to constitute iron, properly so called, and the product is raw or blistered steel. The casting which does not contain any manganese loses by the effect of combustion a portion of silica proportionable to the quantity of carbon burnt, and furnishes iron only as a definitive product.

It is simply to the mechanical action of the hammer that the distinctive features of steel, as compared with cast metal, are due. In order to effect this change, the blistered steel is broken into pieces and melted down; they are afterwards tempered, again broken into pieces, and welded together at a good welding heat. The steel will be the more malleable, and possess more tenacity and uniformity of texture, in proportion to the number of times these operations are repeated. The product is called "wrought or shear steel."

Steel of Cementation and Cast Steel.—When bar iron is heated to a white heat, or even melted in close vessels containing coal or carbonaceous substances, it takes up a certain quantity of carbon, and is transformed into castings of various kinds.

If the iron contains, together with silica, phosphorus and arsenic in proportions suitable for softening the granular particles of iron during their combination with the carbon, by keeping it for a certain time at a red heat with powdered charcoal, a casting is obtained, which, when submitted to the action of the hammer or of rollers, furnishes a product known as "steel of cementation." During this operation, the stratum of oxide which covers the particles of iron inside loses its oxygen, and passes again into a metallic state; but the vacant spaces occasioned by this are filled up, as the ferruginous particles, which are in a semifluid state, reassume the crystalline form. The carbonic oxide gas in escaping forms large blisters on the surface of the metal, under which the softened mass crystallizes. On being broken, the interior of these blisters, instead of appearing of a dark colour, indicating the presence of a stratum of protoxide, presents a brilliant and rainbow-tinted appearance, the yellowish and bluish tints distinguishing bronzed steel being observable. If this steel be wrought at a white heat, these blisters will weld in with the mass with the greatest facility. During cementation the carbon combines with the component particles of the iron in various proportions, depending in a great degree upon the chemical composition of those particles. It is therefore a vulgar error to suppose that steel of cementation contains more carbon at the surface than in the interior, as stated in all technological treatises. Thus, in the best Dannemora steel, it very frequently happens, when the cementation is finished, that the centre of the metal contains a much greater quantity of carbon than in the superficial portions. It may also happen that steel produced from the best Dannemora bar iron will

differ in an extraordinary manner as regards hardness in various portions of the bar; and for this reason, in steel works in England, the bars of steel are always broken into several pieces, in order to class those pieces together which are the most similar in quality.

If ordinary iron be submitted to cementation, that is to say iron in which the proportion of silica is ordinarily insignificant when compared with that of carbon, and if independently of this the iron is deficient in the quantity of phosphorus and arsenic necessary for easily softening the metallic molecules, only carburet of iron and a little siliciuret of iron are produced, but the carbon does not combine with the silica. In this case the steel obtained is deficient in malleability and tenacity, for this reason, that the molecules will not unite or crystallize until they have taken up a quantity of carbon more than sufficient to produce steel. With regard to simple carburetted iron (when it contains more carbon), it either will not harden at all when tempered, or becomes friable and brittle when heated to redness, even when it does not contain more carbon than steel of good quality.

The fracture of the steel of cementation, now under notice, is gray and dull, while steel of good quality is of a silvery aspect, and presents cubical crystals.

The best steel can only be obtained by the cementation of forged iron. Whilst the metal is combining with the carbon, the iron must not enter into a complete state of fusion, as in that case groups of crystals, each possessing a different degree of carbonization, would be formed; even the best Dannemora iron will not furnish a uniform product fit for purposes of commerce when melted with substances containing carbon. I am well-aware that the experiments of Clouet, Hachette and Breant may be opposed to me, as set forth in various treatises upon chemistry; but these are unfortunately mere laboratory experiments, the authors of which have prudently concealed, or passed over in silence, all those which were unsuccessful. When the operator has obtained a regulus at the bottom of his crucible, and when, after immense trouble, he has succeeded in extracting from it a small portion of steel capable of being worked, he immediately hastens to publish his pretended discovery in some journal, of which others become faithful and credulous echoes; thus, since the manufacture of steel has become the subject of chemical inquiry, complaints are daily becoming more frequent upon the difficulty of procuring steel capable of resisting the treatment to which it is subjected in the arts. If the persons who preside over the coining department either at London or Munich were consulted, they would all agree in saying that it is now very difficult to meet with the quality of steel necessary for making the dies. Even in England good steel becomes more and more scarce. With regard to the manufactories of cemented or cast steel established upon the continent, they furnish products the quality of which is so uncertain, that the workman is often reduced, after having lost his time and trouble, to throw certain portions away, as they want the necessary uniformity and tenacity.

All the artificial alloys of silver with steel, of which so much has been said, are not fit for anything, and are never met with in commerce.

When the steel has been withdrawn from the cementing furnace, and after it has been broken and the pieces drawn out, they are submitted to one of the two following operations:—The pieces, after being sorted, are piled one upon the other and welded together (this is called faggoting the steel); or the sorted pieces are placed in clay crucibles of a nearly cylindrical form, and cast in a reverberatory furnace, in which two crucibles are placed, one behind the other, upon cakes of fire-clay; the orifice of these crucibles is closed by a flat cake of fire-clay. The bars of cemented steel, as above mentioned, are divided into pieces of 1 or 2 inches in length; these pieces are distributed, according to their degree of carbonization, in vessels fixed to the walls of the place in which the melting is carried on.

These different qualities of steel are generally combined in such a manner as to obtain a product the best suited for the purposes to which cast steel is ordinarily applied.

In all treatises on practical chemistry it is asserted that, in order to melt steel, it is to be covered with a layer of glass or blast furnace slag; that the opening of the crucible is luted, or at least becomes firmly fixed during the operation; these assertions are however erroneous. In the first steel manufactories in Sheffield, steel only is put into the crucibles. With regard to the cover, it is evident that it must not adhere to the crucible, as it is necessary the operator should remove it from time to time with a bar of iron, in order to ascertain the state of the metal.

In order to obtain steel of the best quality, it is not sufficient that the melted mass be run into moulds; the most essential point is to make the casting at the proper time, and for this purpose the operator must be guided by the quality of the steel. This is the duty of the workman, who from long practice can tell the suitable point of fusion, either by simple inspection or by means of his bar of iron, with which he merely touches the surface of the metal, being most careful not to plunge it into the melted mass. As the quality and uniformity of the steel depend in a great measure upon the experience and judgement of the workman who directs the casting, it follows that, even in England, a good caster is much sought after and well-paid.

It is not difficult therefore to explain why so many of the attempts made to establish manufactories of cast steel in Germany have failed, and will again fail. Thanks to the errors propagated by technical works, and by the assertions of superficially informed travellers, who had frequently been purposely deceived, it was imagined that in order to obtain English steel of good quality, it was only necessary to melt cemented steel in a crucible, and afterwards pour it into moulds when in a state of fusion.

As soon as a crucible is emptied, it is replaced in the oven; each crucible serves for one day's work, *i. e.* four or five castings, after

which it is thrown aside. For ordinary purposes, the steel is run into cast iron moulds of a prismatic form, previously heated and closed. When the steel is required for making saw-blades, plates, &c., it is run into large moulds of a parallelopiped form. Steel which is very hard and highly carbonized, contracts considerably in the moulds; great skill is therefore required to run it into the moulds in such a manner that no vacuum may be produced. In that part of the prism corresponding to the jet, a funnel-shaped aperture from 1 to 2 inches deep is formed; this is detached and melted down with other pieces of steel.

The transverse fracture of a prism of hard steel is silvery, and has a number of rays radiating from the centre; steel less hard is, on the contrary, of a uniform granular and crystalline texture. This steel possesses all the brittleness of cast metal.

By fusion, steel of cementation acquires peculiar properties, and does not sweat so much as before casting.

When steel is produced from iron of bad quality, and carburets of a different nature are produced during cementation, the melting, instead of improving it, renders it much worse; as, in that case, the different carburets of iron, which are of inferior quality, separate still more during cooling. This has given rise to an old saying, well-known among English founders, that "when the devil is put into the crucible, nothing but the devil will come out."

It is to the existence of these heterogeneous metallic carburets, which are produced during cementation in iron of inferior quality, and which form new combinations during the fusion of the metal, that the complaints of workmen working in steel are to be attributed. In fact, these carburets being only, so to speak, agglutinated, even in bars of forged steel, each of them, at the moment of tempering, is contracted or dilated more or less than the one immediately adjoining it, so that from that time a separation commences between the unequally carbonized layers; in other words, a flaw or crack is produced, which may be distinguished by a peculiar noise at the moment when the steel is plunged in the water, or at least there is a tendency to separation, which only requires the cooperation of an exterior cause, such as a shock, to effect it. This is often observed in razors, &c.

The transverse fracture of cast steel ought to present a perfectly homogeneous surface when the bar is broken by a sharp blow, after being cut or marked with a chisel. The slight inequalities which are perceptible ought to be undulating, and to blend insensibly at their bases with the rest of the metallic surface. When, on the contrary, they stand out perpendicularly, the conclusion may be arrived at, that this portion of the bar was the point of contact of two unequally carbonized layers, which, by separating either at the moment of tempering or at a later period, had inevitably given rise to this rupture.—*Revue Scientifique et Ind. du Dr. Quesneville.*

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

May 4, 1846. (The President, Professor Graham, in the Chair.)
The following papers were read:—

“Researches on Coumarine,” by Dr. Bleibtreu.

The first part of this communication refers to a careful chemical examination of the crystalline matter from the *Asperula odorata*, or woodruff, a plant remarkable for the very agreeable odour it acquires after drying, and which is employed in Germany in the preparation of a favourite beverage, the *Maiwein*. After referring to the experiments of preceding chemists, the author describes the process by which the principle in question was extracted. The plant was exhausted by boiling alcohol, the alcohol distilled off from the strained liquid, and the syrupy residue boiled with water, which left undissolved chlorophyll and other matters. On agitating the aqueous solution with æther, and allowing the latter to evaporate, a crystalline substance was obtained, which, when purified by repeated crystallization, possessed in every respect the properties and composition of coumarine. It was convertible by fusion, with hydrate of potash, into salicylic acid.

Some little discrepancy, however, between the analytical results obtained and those of Delalande on coumarine from Tonka beans, induced Dr. Bleibtreu to repeat his analyses on the substance derived from the last-named source. The coumarine was extracted by alcohol from the beans, and carefully purified, especially from an oily matter, often present in considerable quantity. The analyses agreed exactly with those of the coumarine from the *Asperula*, and led directly to the formula $C^{18}H^6O^4$, instead of $C^{18}H^7O^4$, adopted by Delalande.

The coumaric acid of that author was then examined. It is prepared by acting upon coumarine by highly concentrated solution of potash, at a high temperature. There is no disengagement of hydrogen. The acid contains $C^{18}H^7O^5$, HO , and consequently differs only from coumarine by the elements of water. Unless very carefully purified, it is apt to retain traces of undecomposed coumarine on the one hand, or of salicylic acid on the other.

A crystallizable substance called *nitro-coumarine*, prepared by the action of nitric acid upon coumarine, is next described. Its preparation requires much care, or it is contaminated by picric acid, which is readily formed under the circumstances. Nitro-coumarine contains $C^{18}\left\{\begin{matrix} H^5 \\ NO^4 \end{matrix}\right\}O^4$, or coumarine in which an equivalent of hydrogen is replaced by the elements of nitrous acid.

The *Melilotus officinalis*, and the *Anthoxanthum odoratum*, or sweet-smelling vernal grass, also contain coumarine, to which they owe their odour.

“On the Solvent Action of Drainage-Water on Soils,” by John Wilson, Esq.

The object of the author in this paper is to show the advantages likely to arise from the use of manures less readily soluble in water than those usually employed, or to divide the gross quantity of manure requisite for one season, and to apply it in small portions, and as frequently as the nature of the crop will admit. From the quantity of valuable saline substances and organic matter removed by the drainage-water, as shown by numerous analyses, the author urges the necessity of preserving this, and returning it again on the soil by irrigation.

"On the Influence of different Kinds of Food in the Production of Milk and Butter," by R. D. Thomson, M.D.

After cursorily reviewing the opinions of Beccaria, Prout, Liebig, Dumas and Boussingault on this subject, and stating the importance of the settlement of the question to the agriculturist, the author proceeds to give the results of an extensive series of experiments on the effect of different kinds of food as nourishment. The investigation was carried on with two cows (a description of which is given) during 3½ months. The milk produced, food consumed, butter extracted, and the dung, were all accurately noted down for each cow, and are arranged in a series of tables. Proximate analyses of the various kinds of food consumed and of the dung are given, showing the quantity of wax and oil contained, as also of the milk and butter produced by each cow. Ultimate analyses are also given of the food and dung, to exhibit the nitrogen consumed. Ash analyses of the various foods are likewise appended. Table I. grass; II. barley crushed; III. malt; IV. a mixture of barley and malt; V. a mixture of barley and linseed; and VI. beans, were successively tried. The following table exhibits the milk and butter from these respectively, on an average of five days:—

	Grass.	Barley.	Malt.	Barley and and malt.	Barley and linseed.	Beans.
Milk	114.0	107.0	102.0	106.0	108.0	108.0
Butter	3.5	3.43	3.2	3.44	3.48	3.72
Dung dried at 100°..	33.6	34.6	31.6	38.0	34.6	31.5
Nitrogen in food....	2.3	3.89	3.34	3.6	4.14	5.27

Thus it is shown that grass yields the largest quantity of milk, and nearly the greatest weight of butter, and contains no oil; and that beans, which contain the next smallest amount of true oil, afforded the greatest weight of butter. It will be seen also that, with the exception of grass, the butter increased with the proportion of nitrogen in the food. This exception as respects grass the author endeavours to explain away on the ground that it contains the ingredients necessary for the system in their proper relations. These ingredients Dr. Thomson classes as the albuminous or nutritious, destined for supplying the waste of tissues and the nutrition; and the calorificent, or portion absolutely necessary for keeping up the animal heat by respiration; and considers that it is upon their relation, as applied to the varied conditions of animals, that the true system of dieting depends.

THE CHEMICAL GAZETTE.

No. XC.—July 15, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Nitric Acid upon Choloidic Acid and Cholesterine.
By Prof. J. REDTENBACHER.

THE following researches were undertaken, in the first instance, for the purpose of obtaining some more accurate knowledge of the nature of cholesterine by studying the products of its decomposition. In the course of the examination, one of the ultimate products of the decomposition of cholesterine appeared to stand in some relation to the bile; and for this reason similar experiments were instituted with the unnitrogenized portion of bile, which latter I shall first describe.

Action of Nitric Acid on Choloidic Acid.

The choloidic acid used was prepared in the manner proposed by Demarçay*. Bile, freed from mucus and fat, was boiled with tolerably strong hydrochloric acid, until the whole of the choloidic acid had separated. It was pulverized and well-washed with water.

The experiments of Theyer and Schlosser† have shown that, during this process, the dyslysine of Berzelius is produced, and that this body only differs from choloidic acid in containing 4 atoms less of water. As my object was to examine the products of oxidation of the unnitrogenized portion of bile, it was evident that I must obtain similar products from choloidic acid and dyslysine.

When choloidic acid is gently warmed with tolerably strong nitric acid, a violent action ensues, and the mass rises very considerably; the same takes place at common temperatures with concentrated acid, and is attended by a copious emission of nitrous fumes. The same products result from either acid.

A quantity of choloidic acid was drenched in a large beaker glass with concentrated nitric acid. After the first violent action, the choloidic acid was transformed into a soft yellow resin, and partially dissolved in the nitric acid. The fluid mass was poured into a capacious retort, fitted to a cooling apparatus and receiver, and about four-fifths of the nitric acid distilled off at a moderate heat. If nitrous vapours had not ceased to be evolved, the distilled acid was

* Liebig's Annalen, xxvii. 287.

† *Id.*, l. 239.

poured back into the retort, with occasionally an additional quantity of fresh acid.

When nitric acid produced no further action, the whole quantity of the distilled acid was mixed with twice its volume of water, again poured over the residue in the retort, and redistilled. By the first of these operations, it was intended that the choloidic acid should be as highly oxidized as possible; by means of the last, the whole of the volatile products separated from the residue in the retort, and collected in the receiver.

There remained in the retort a yellowish-white, soft, pasty mass, partially soluble in water, crystalline, and still mixed with much nitric acid.

Volatile Products.

A colourless, or from nitrous acid pale bluish-coloured liquid, had collected in the receiver, still mixed with much nitric acid, and possessed of a powerfully penetrating, stupefying smell. On the surface of the fluid floated drops of a fatty substance; at the bottom of the retort was a heavy oil, possessing and causing the penetrating odour.

In order to separate the volatile products, the acid liquid was poured off from the heavy oil. It contained a considerable quantity however in solution, which distilled over at a low temperature, accompanied by deutoxide of nitrogen.

The whole of the acid liquid from which the heavy oil had separated was very nearly neutralized with potash or soda, leaving it a very slight acid reaction. In this manner the nitric acid was fixed, and could be separated from the acid volatile products. The product of this distillation was richer in the fluid fatty body, and smelt of acetic acid and cheese. The layer of fat oil was drawn off with a pipette, the fluid containing acetic acid diluted with water, and shaken with different portions of æther, to remove fatty matters.

Acetic Acid.—The acid liquid, after treatment with æther, had all the properties of a dilute solution of acetic acid, and in addition a faint smell of cheese; it was therefore necessary to examine it more closely, as metacetic and acrylic acids smell in the same manner of cheese. On neutralizing the acid with ammonia, and precipitating whilst hot with nitrate of silver, the crystals which formed had not the form of pure acetate of silver, nor could pure acetate be obtained except by saturating the acid with carbonate of soda, purifying the acetate of soda by recrystallization, and then precipitating with nitrate of silver. The analysis of the silver salt thus obtained proved it to be pure acetate.

Fatty Acids.—The layer of light fatty oils was distilled in a small retort, and the first portion which passed over, containing water and traces of acetic acid, collected in a separate vessel; the last portions were also rejected, and only that which came over about the middle of the operation was used for the experiments. This product was colourless, had a rancid taste and smell, and became in part solid at 32°. In water it was difficultly soluble, freely in alcohol; both solvents

acquired an acid reaction, and the latter an agreeable fruity odour. At a temperature above 212° it distilled over unchanged. It combined easily with caustic and carbonated alkalis and alkaline earths to soluble salts; with the heavy metallic oxides, to insoluble salts.

This light fatty oil possessed all the properties of the volatile fatty acids, as they are obtained from butter. It was easy to foresee that the substance did not consist of a single acid, but was a mixture of several. To separate and analyse singly each of these fatty volatile acids in the usual manner, by forming barytic salts and crystallizing one compound after the other, would have required more material than was at my disposal; but as it is known that the hydrates of the volatile fatty acids contain carbon and hydrogen in equal equivalents, and only differ from each other in the relative proportions of oxygen,—if, on analysis of any mixture of such volatile acids, the equivalents of carbon and hydrogen are found to be equal, and the atomic weights and physical properties of the barytic salts obtained (without actual elementary analysis of each) are observed to be in accordance, we can with sufficient certainty affirm the presence of certain volatile acids in the mixture.

Upon this assumption I analysed the mixture of volatile oily acids, and obtained the following empirical formula:—

	Calculated.		Found.
15 equivs. carbon	1137·8	65·96	66·01
15 ... hydrogen	187·2	10·86	10·86
4 ... oxygen	400·0	23·18	23·13

The carbon and hydrogen are therefore actually as C : H; and if the empirical formula above be doubled, it will contain the elements of capric and valerianic acids, $C^{30}H^{30}O^8 = C^{20}H^{20}O^4 + C^{10}H^{10}O^4$.

The remaining portion of the distilled fatty acids and the residue in the retort was saturated with baryta water, and boiled with water until everything was dissolved with the exception of a small quantity of carbonate of barytes.

From the hot solution a difficultly soluble salt of barytes crystallized on cooling in scales of a silky lustre. It was repeatedly crystallized, and each time the first portions only taken. This salt had the appearance, the solubility, as well as the properties of caprate of barytes.

Its atomic weight also was in accordance:—

	Calculated.	Found.
Caprate of barytes, atomic weight . .	3011	2983
Anhydrous acid	2054	2027
Barytes per cent.	31·78	32·07

The liquid from the caprate of barytes deposited on evaporation an indistinctly crystallized salt, having the appearance of a mixture of caprate and caprylate of barytes; it was not further examined; but on again concentrating the mother-liquor, granular crystals resembling poppy seeds separated, which on being decomposed by an acid gave off the smell of perspiration peculiar to caprylic acid.

The atomic weight proved these to be caprylate of barytes :—

	Calculated.	Found.
Caprylate of barytes, atomic weight . .	2657	2656
Anhydrous acid	1701	1699
Barytes per cent.	36·01	35·95

Sufficient caprylate of barytes crystallized to afford a silver salt.

Caprylate of silver is a white cheesy precipitate, not quite insoluble in water. It was pressed and dried at 212° without blackening, and gave on analysis the following formula :—

	Calculated.		Found.
16 equivs. carbon	1213·7	38·50	38·55
15 ... hydrogen	187·2	5·93	6·01
3 ... oxygen	300·0	9·52	9·22
1 equiv. oxide of silver	1451·6	46·05	46·22
1 ... caprylate of silver	3152·5	100·00	100·00

In the preparation of caprate and caprylate of barytes, a salt in minute scaly crystals of a pearly lustre was often obtained, which retained the same form when often recrystallized, and led me to conjecture that it might be the salt of an acid so constituted as to form a medium between the capric and caprylic acids, or containing only 18 equivs. of carbon; on analysis, however, it showed itself to be of so changeable a nature, although always taking a position between the two acids mentioned, as to render it probable that it was a mixture of the salts of the two acids.

The mother-liquor, from which the caprylate of barytes was separated by filtration, was coloured yellow, no longer limpid, and smelt strongly of cheese; not a trace of caproate of barytes could however be obtained from it. On allowing it to evaporate slowly in the sun, a barytes salt, in large crystalline laminae with the lustre of mother-of-pearl, was deposited, which had much resemblance to butyrate of barytes; it was with difficulty obtained pure by recrystallization, and its atomic weight found to exceed that of butyrate of barytes by 100.

Its atomic weight was found most nearly to correspond with valerianate of barytes :—

	Calculated.	Found.
Valerianate of barytes, atomic weight	2127	2107
Anhydrous acid	1170	1150
Barytes per cent.	44·97	45·41

The properties of this salt resemble as much those of butyrate as those of valerianate of barytes, both of which salts however differ but little from each other. It is probable that butyric acid was also present amongst these products, but from its greater solubility always constituted the mother-liquor, was imbibed by the bibulous paper used in drying, and thus lost. Two salts which were examined gave for the acid an atomic weight between that of valerianic and butyric acids.

The atomic weight found for the silver salt was ..	2570
... .. of valerianate of silver.....	2622
... .. of butyrate of silver.....	2445
The atomic weight of the barytes salt	2085
... .. valerianate of barytes.....	2127
... .. butyrate of barytes.....	1952

Heavy Oil.—The heavy oil which collected at the bottom of the receiver, and was partially dissolved in the fluid product of distillation, was, after rectification, well-washed with water, in which it is very little soluble, in order to free it from adherent acids. It presents itself then as a clear, very slightly yellow, oily fluid, of much higher specific gravity than water. It has a very powerfully penetrating and stupefying smell, provoking tears, and after longer action causes headache, so that its poisonous properties cannot be doubted. It has an acid reaction, on being heated gives off brown vapours of nitrous acid, and if the temperature be raised to 212° , it detonates with a moderate explosion and a blue flame. It is but little soluble in water, readily in alcohol, and itself dissolves fats and fatty acids.

If this oil be treated with an alkali, ammonia or potash, it becomes instantly coloured yellow; and if the alkali was concentrated, precipitation of a lemon-coloured salt in crystals immediately follows. The oil does not disappear entirely, nor does its peculiar smell at first; but when allowed to stand for some time, this is succeeded by a still very penetrating cinnamon-like smell, which does not stupefy.

The original oily body is therefore separated by alkalies into an acid, which I call nitrocholic, and which combines with the alkali, and into another neutral oil, which I call cholacrole. The original oily body was not analysed, as all proof of its purity was wanting. During its formation and redistillation, it dissolves fatty acids, which can only be separated from it by an alkali. For determining the composition of nitrocholic acid, I chose the potash salt. The acid forms, however, crystallizable salts with the other alkalies. When the original oil has stood for some days with a dilute solution of potash, the yellow solution of nitrocholate of potash is poured off from the cholacrole, which remains as an oil at the bottom of the vessel. On slowly evaporating the potash salt, it crystallizes in distinct crystals. All heat must be avoided during evaporation, as it decomposes the acid. It is best to evaporate over sulphuric acid *in vacuo*. When most of the nitrocholate has crystallized, there remains a yellow uncrystallizable mother-liquor, which smells of butter. If it be decomposed by dilute sulphuric acid, brown vapours of nitric acid go off, drops of oil which smell strongly of fat are formed, and there is a distinct smell of prussic acid produced. If this last mother-ley be treated with alcohol, a potash salt resembling those of the fatty acids is dissolved, and generally nitrate of potash remains.

Nitrocholate of potash is lemon-yellow coloured, crystallizes in the form of yellow prussiate of potash, has a peculiar, slightly stu-

pefying smell, and is not permanent in the air; for as soon as the crystals are dry, they fly into a number of small pieces. The same occurs more quickly when they are warmed, and if heated to 212° they detonate; they are not more permanent when dried *in vacuo*. If the solution of the salt is boiled for some time, crystals of nitre are obtained; if sulphuric acid is added to the solution, the same products are obtained as from the mother-liquor above. With solutions of metallic salts, no precipitates are produced by nitrocholate of potash. The preparation of this salt does not always succeed; in its stead I obtained sometimes rose-red and violet crystals of a potash salt and much prussic acid. As nitrocholate of potash cannot be dried perfectly without decomposition, I selected large crystals, pressed them between blotting-paper, and endeavoured with these to determine approximatively its composition:—

	Calculated.	Found.
Atomic weight of nitrocholate of potash	2362	2381
... .. anhydrous acid	1772	1791
Potash per cent.	24.97	24.78

In burning with oxide and phosphate of copper, to drive out the carbonic acid from the potash, I found it difficult, notwithstanding the presence of metallic copper in the front part of the tube, to avoid the evolution of deutoxide of nitrogen. The results of several combustions showed the probable composition of nitrocholate of potash to be—

	Calculated.		Found.
2 equivs. carbon	151.7	6.42	7.91
1 equiv. hydrogen	12.5	0.53	0.59
4 equivs. nitrogen	708.2	29.98	29.98
9 equivs. oxygen	900.0	38.19	
1 equiv. potash	589.9	24.17	24.78
1 equiv. nitrocholate of potash	2362.3	100.00	100.00

The formula $C^2 H N^4 O^9 + KaO$, considered as a group of elements analogous to carbazotate of potash, can be represented as $NO^2, KaO + NO^4 (C^2 N^2 H^2)$; by means of which formula the usual products of decomposition, nitric acid, nitrous acid and prussic acid, are partially pointed out.

The oil remaining at the bottom of the vessel, in the preparation of the nitrocholate of potash, is cholacrole. It should be shaken with water until neutral, and is then a faintly yellow-coloured oil, with a penetrating, stupefying smell, resembling that of cinnamon, soluble with difficulty in water, but readily in alcohol and æther. It is not only neutral, but quite indifferent, both towards potash and acids. Heated to 212° , it is decomposed with evolution of nitrous acid. It frequently burns, giving rise to a slight detonation, without access of external oxygen, leaving a small quantity of fluid smelling of fat.

The analysis of cholacrole, dried over chloride of calcium, gave the following as its composition:—

	Calculated.		Found.
8 equivs. carbon	606·8	26·12	26·15
5 ... hydrogen	62·4	2·69	2·81
2 ... nitrogen	354·1	15·24	15·28
13 ... oxygen	1300·0	55·95	55·76
	2323·3	100·00	100·00

Non-volatile Products.—Mention has already been made of a thick brownish-yellow mass, containing still much nitric acid, which remained in the retort after the separation of all the volatile products of the oxidation of choloidic acid. This residue, on being poured out, separates into two layers; a soft crystalline body, like froth, comes to the top, which I call choloidanic acid, and below it is a thickish yellow-brown, very bitter liquid. The choloidanic acid can be separated by a funnel with powdered glass, dissolved in boiling water, and purified by recrystallization. Choloidanic acid crystallizes in long, brilliant, white, hair-like prisms; dried on a filter, they shrink together, and form a thin film resembling asbestos. It is very porous and light, almost insoluble in cold water, and not readily soluble in hot; the solution is acid. In alcohol it is more easily soluble, and crystallizes on evaporation in small granular crystals. It dissolves without change in nitric and hydrochloric acids. At 212° it loses no weight; at a higher temperature, it melts, blackens, and gives off a bitter and irritating vapour, leaving a coaly residue; ignited, it burns with a smoky flame. The salts formed with alkalis, earths, and heavy metallic oxides, are insoluble or difficultly soluble.

Four analyses of choloidanic acid gave the following results:—

	Calculated.		I.	II.	III.	IV.
16 equivs. carbon ..	1213·7	58·82	58·31	58·42	58·54	58·57
12 ... hydrogen	149·8	7·26	7·25	7·59	7·45	7·58
7 ... oxygen ..	700·0	33·92	34·44	33·99	34·01	33·85
1 equiv. choloidanic acid	2063·5	100·00	100·00	100·00	100·00	100·00

The alkaline salts of choloidanic acid do not crystallize; to obtain those with the heavy metallic oxides, the acid must be saturated with ammonia, and precipitated by the respective salts of the metallic oxides. These are all flocculent precipitates, which are easily filtered, but all more or less decomposed by water, some of the acid being removed by each successive washing. For this reason it was not possible to determine accurately the atomic weight of the acid.

The mother-liquor separated by filtration from the choloidanic acid contains two or three substances besides nitric acid. One of these separates in flocks on diluting the thick fluid with water, which collect to a soft resinous body, and render the water milky. This resin appears to be only choloidic acid not completely oxidized; it decreases in quantity by renewed boiling with nitric acid, but is difficult to remove altogether. I did not examine it further, but

was enabled to free the mother-liquor from it by repeatedly adding water, filtering and evaporating, until on diluting with water the fluid remained clear. There remains still in the mother-liquor oxalic acid, and another soluble, not crystallizable acid, forming the chief product of the oxidation of choloidic acid, and which, for reasons to be given below, I call cholesteric acid. It was found, on endeavouring to separate it from oxalic acid, that the same metallic oxides produced with both acids, salts of equal solubility, oxide of silver alone forming an exception; oxalate of silver being insoluble in water; cholesterate of silver, soluble, although with difficulty, in the mother-liquor from which it is precipitated. The whole mother-liquor therefore, containing both oxalic and cholesteric acid, is saturated with ammonia, and nitrate of silver added in excess. It is then boiled with the copious precipitate, a part of which dissolves; and after filtering off the insoluble portion, and allowing the solution to cool, a crystalline crust of cholesterate of silver is deposited. It was decomposed with sulphuretted hydrogen, warmed and filtered. The solution contains cholesteric acid, which on evaporation becomes thick and agglutinates to a gummy mass, which cannot be perfectly dried, nor could it by any means be made to crystallize. Cholesteric acid is a light yellow gum-like mass, and attracts moisture from the air, becoming soft. It has a tolerably acid, astringent, bitter taste, forms a yellow solution with water, alcohol and acids; heated in a closed tube, it is decomposed, and gives out a brown, penetrating, bitter vapour, leaving a residue of charcoal; with access of air, it burns with a smoky flame. Its chemical reactions resemble very much those of choloidanic acid. The salts it forms with alkalis and alkaline earths are soluble and not crystallizable. The precipitates with metallic oxides have often a tinge of yellow; the precipitate with oxide of iron is yellowish-brown; with copper it is siskin-coloured.

Cholesterate of silver was found to have the following composition:—

	Calculated.		Found.
8 equivs. carbon	606·8	24·19	23·70
4 equivs. hydrogen	49·9	2·00	2·23
4 equivs. oxygen	400·0	15·94	15·82
1 equiv. oxide of silver	1451·6	57·87	58·25
1 equiv. cholesterate of silver	2508·3	100·00	100·00

The formula of cholesteric acid, compared with those of the known acids, is found to correspond with that of pyrogallie acid (Campbell). The properties of the two acids are however quite distinct.

With cholesteric acid, the series of products of the action of nitric acid on choloidic acid is finished. In point of quantity this acid is the chief product; then follow acetic acid, choloidanic acid, the fatty acids, and last and least in quantity, the bodies containing nitrogen.

Theyer and Schlosser, in their interesting paper on the bile*, ob-

served also the production of the fatty acids and of a crystalline substance, by the action of nitric acid upon the whole bile. There is no doubt that the crystalline body they obtained was choloidanic acid; but as they crystallized it from alcohol, they obtained it contaminated with a little of the resinous body, which is precipitated by water. The analysis of the silver compound of their acid gave the same relative proportions of carbon and hydrogen; but the analysis of the hydrated acid showed, on account of that impurity, a little too much carbon and hydrogen for pure choloidanic acid.

By the foregoing experiments, a new source of the fatty acids has been shown, and it might perhaps be thought probable that their formation was due to fat coexisting with the other constituents in the bile. As however Laurent and Bromeis*, in their examination of the products of oxidation of the fatty bodies, always found suberic acid to be the chief product, and not a trace of this easily recognised acid was perceptible throughout my experiments, we have every reason to believe that these volatile fatty acids are true products of the oxidation of choloidic acid, and that the fats are not the only source from whence they can be obtained.

At a future opportunity I shall likewise show that oleic acid yields a number of volatile fatty acids when acted on by oxidizing agents, but that in that case also suberic acid is invariably the chief product. Liebig's theory of the formation of fat is quite in accordance with this new fact. The experiments of Pelouze and Boussingault have clearly shown that the unnitrogenized food is capable of conversion into fatty substance. My results show that the same may be the case with the unnitrogenized portion of the bile.

Action of Nitric Acid on Cholesterine.

Cholesterine, which is generally classed by chemists amongst the fats, although it only resembles them in outward appearance and is not saponifiable, was found by Pelletier and Caventou† to yield, when acted upon by nitric acid, a crystallizable acid, which they called cholesteric acid (*acide cholesterique*). This acid contained nitrogen, and should more properly have been called nitrocholesteric acid. However, since the time of its discovery nobody has again been able to produce it. I myself have tried, by modifying the process in all manner of ways, to obtain it, but without success. I could never obtain even a trace of a crystallizable compound.

In oxidizing cholesterine by nitric acid, I adopted the same mode of procedure as with choloidic acid; no action takes place in the cold, but on the application of heat the action soon becomes violent; a resinous matter is formed, which dissolves in the acid. The acid was returned into the retort, as with choloidic acid; and to obtain all the volatile products, the last portion was mixed with water. In the receiver were found acetic acid, with traces of the volatile acids of butter; they were separated by the same method as before. The volatile acids were formed in such minute quantity, that I could

* Liebig's *Annalen*, xxxv. 86.

† *Annal. de Chim. et de Phys.*, vi. 401. Liebig's *Annalen*, vi. 24.

only prove their presence by converting the acetic acid into acetic æther, which was always accompanied by the peculiar odour of butyric and caproic æther. The non-volatile products were of precisely the same nature as those obtained from choloidic acid. The chief product was the uncrystallizable gum-like substance which was obtained above, mixed with oxalic acid, and which from its occurrence here I called cholesteric acid.

The cholesterate of silver has the following atomic weight:—

	Calculated.	Found.
Atomic weight of cholesterate of silver ..	2508	2524
... .. the anhydrous acid	1056	1072
... .. oxide of silver per cent.	57·87	57·51

The analysis gave as its composition—

	Calculated.		Found.	
			I.	II.
8 equivs. carbon	606·8	24·19	23·54	24·26
4 equivs. hydrogen	49·9	1·99	2·24	2·38
4 equivs. oxygen	400·0	15·95	15·95	15·85
1 equiv. oxide of silver	1451·6	57·87	57·51	57·51
1 equiv. cholesterate of silver	2508·3	100·00	100·00	100·00

Choloidic acid and cholesterine therefore give the same products of oxidation; and it follows from this that cholesterine is related to the unnitrogenized portion of the bile, and not to the fats and fatty acids.—Liebig's *Annalen*, lvii. 145.

Method of separating the Body produced by the joint Action of Sulphuric Acid and Sugar on Ox-Bile (Petténkofer's Test). By GEORGE KEMP, M.D. Cantab., F.C.P.S.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

The very remarkable discovery of Petténkofer, that, by treating bile with sulphuric acid, and then adding a small portion of syrup, a peculiar colour is immediately produced, has afforded one of the most characteristic and elegant tests for the biliary fluid hitherto presented. It appears however that the discoverer was not fortunate in his attempts to isolate the new body; and from a conviction that, if this could be accomplished, we should not only be furnished with a substance extremely interesting to the chemist *per se*, but important as developing a remarkable and previously unsuspected reaction, and of great value as furnishing the means of deciding the real nature and composition of the bile beyond all contradiction, the writer was induced some months ago to direct his attention to the subject, and has only deferred making the results public from the intention of accompanying the method of separation with the ultimate analyses. Other subjects have however intervened, which may postpone the investigation for some weeks; and he therefore ventures to present it to the chemical public in its unfinished state.

Having evaporated ox-bile in a water-bath to the consistence of

a thin syrup, add an equal bulk of alcohol, spec. grav. 0·840, and strain through linen. The object of this operation is to separate the mucus; but, as all who have worked on this subject are aware, the filtration goes on very sluggishly. This may be obviated by the following artifices. While adding the alcohol, keep stirring briskly; the bubbles of air, which are mechanically mixed with the fluid, attach themselves to the mucus, which is coagulated by the alcohol; and thus the largest portion floats on the top, and may be removed by a spatula or spoon; if, in addition, the strainer be moistened, and then sprinkled over with pure quartz sand, the filtration will go on very satisfactorily. The strained fluid is now introduced into a retort, and the alcohol distilled over in a water-bath; to the residue add a quantity of syrup, which of course cannot be accurately determined until the analyses are completed; but one-eighth of the bulk answers very well; and when cool pour concentrated sulphuric acid into the retort until the whole is converted into the peculiar coloured fluid obtained by Pettenkofer's treatment. Water is now added until the colouring matter separates in the form of a bulky chocolate-coloured precipitate. The reason that the discoverer failed to isolate the body appears to be, that it is soluble in the strongly acid solution, and it is not until this is very greatly diluted that the precipitation occurs; with precaution, however, the resulting fluid is obtained perfectly colourless. The precipitate may now be separated by straining through linen.

This plan is sufficient for ordinary pathological and physiological purposes, but for chemical investigation more care is necessary. In the first place, the fatty acids are left by the above method; and it is therefore proper, as a preliminary measure, to remove them as the writer has described in Erdmann's '*Journal*,' vol. xxviii. p. 160. Again, on the addition of the strong sulphuric acid, although the characteristic reaction speedily occurs, it is preceded by the separation of the substance which was formerly called biliary resin; and, as this also is insoluble in water, a portion of it may remain mixed with the new body. The fluid also is so intensely coloured, that the progress of the reaction cannot be observed. This difficulty however is easily surmounted, as the new substance is very soluble in æther, whilst the body which is called biliary resin, as well as the bile, is quite insoluble.

The compounds of lead, silver and barytes are easily formed; and perhaps the name sulpho-cholic acid will be admitted as a suitable appellation for the new body. It is worthy of remark, that, although the above method holds good in the case of ox-bile, sheep's bile, and the bile of other graminivorous animals, it is not available for the bile of the hog; nor does it seem at all improbable that we are on the eve of establishing a distinction between the secretion obtained from animals of different habits.

The analytical results will be forwarded immediately as completed.

St. John's, Isle of Man, June 4, 1846.

On the Presence of Milk-Sugar in Incubated Eggs.

By M. WINCKLER.

In examining and looking through a number of eggs, Winckler found some which exhibited vascular lines internally, and which were therefore incubated. He boiled them hard, and found, on testing the coagulated albumen, that it was remarkably sweet. On testing for sugar, he found sugar of milk present.—Heller's *Archiv*.

On the Production of Taurine from Human Bile.

By Dr. GORUP-BESANEZ.

Demarçay, and subsequently Theyer and Schlosser, found that the products of the decomposition of ox-bile by mineral acids are,—a resinous acid, free from nitrogen,—choloidic acid; a beautifully crystalline body, containing nitrogen and sulphur,—taurine; and ammonia. By a series of experiments and by ultimate analyses, I have proved, that during the biliary fermentation, *i.e.* the spontaneous decomposition of the ox-bile by the influence of the mucus of the gall-bladder, which acts as a ferment, the bilic acid is decomposed into the same products, *viz.* choloidic acid, taurine and ammonia*; and, as a sequel to these observations, I was anxious to ascertain whether the human bile underwent a similar decomposition, especially as Kemp has asserted that the composition of the human bile is entirely different from that of the ox-bile, and has endeavoured to prove it by ultimate analysis. As is well known, fresh ox-bile is not precipitated by weak acids, as the acetic, but it is when it has putrefied; choloidic acid is precipitated from it; and this formation of choloidic acid shows that the neutral or slightly alkaline reaction, which the bile had at first, is converted into a distinctly acid reaction. The property of being precipitated by acetic acid appears at the same time with the occurrence of this acid reaction. I had frequently noticed an acid reaction in human bile, and I always then found that, after the bile had been freed from mucus, acetic acid precipitated a body which resembled choloidic acid, but the quantity of which was far too small to allow of an ultimate analysis; I could not however for a long time discover taurine in human bile. In putrefied ox-bile, after having evaporated it to dryness and exhausted with strong alcohol, the taurine remains with the mucus insoluble in the menstruum, and may be immediately recognised with the microscope. We thus detect beautiful transparent six- and four-sided prisms with oblique terminal surfaces; these are mixed with an amorphous coagulum (decomposed mucus). The crystals are soluble in water and nitric acid, but, as above stated, not in alcohol. Another method of separating the taurine formed during the fermentation of the bile, consists in dissolving the *fresh* bile, which has been freed from mucus and colouring matters, in water, mixing it with a little intestinal mucus, and allowing it to putrefy. The choloidic acid is

* Gelehrte Anzeigen der K. bai. Akad. der Wissensch., No. xciii., 1845.

then completely precipitated by acetic acid; and by evaporating the unprecipitated portion to dryness and exhausting it with strong alcohol, scarcely anything but taurine remains. Its amount however is always small compared to that of the choloidic acid, for the bile of 10 or 12 oxen thus treated does not yield at the most more than 45 to 60 grs. of taurine. In one experiment, the proportion of taurine to choloidic acid was as 1 to 5. Hence the difficulty in detecting the taurine in human bile, the quantity of which is so very small, and which contains so little of the essential constituent of the bile. I obtained beautiful crystals of taurine from human bile, exactly resembling those from ox-bile, by proceeding thus:—The human fluid was freed from mucus, decolorized with bone-charcoal, evaporated, and dissolved in water to allow it to ferment; the solution was not however clear, but milky. It was again evaporated to dryness, and exhausted with alcohol of 0.90; a crystalline mass remained insoluble; this consisted of chloride of sodium and separate very beautiful crystals of taurine. Taurine from human bile, like that from the bile of the ox, appears under the microscope in the form of transparent, six- and four-sided prisms with oblique terminal surfaces. They disappear when moistened with water and nitric acid.

The discovery of taurine in human bile with the microscope is in my opinion important, because it becomes extremely probable that the composition of the human bile is identical with that of the ox, and that Kemp obtained different results merely because he analysed bile which contained choloidic acid already formed. I have satisfied myself, by numerous experiments, that human bile is very rapidly decomposed. Moreover, Kemp does not appear to have decolorized the bile.—Heller's *Archiv*, Heft i. 1846.

[We have seen specimens of taurine obtained by Dr. E. Ronalds from human bile by the ordinary process (continued treatment with mineral acid), and so far we can confirm the author's statement.—*Ed. Chem. Gaz.*]

On the Nature of Yeast. By Dr. LÜDERSDORFF.

Dr. Lüdersdorff supports the theory that yeast is an organic body, and acts by means of its organs upon sugar, in contradistinction to the theories of its action by mere contact, or by its own state of decomposition inducing a similar state in the saccharine solution, by the following experiment:—

A portion of yeast was rubbed between ground glass plates until the globules of which it is composed could no longer be distinguished by the microscope, and its organic structure therefore was destroyed. An equal portion was exposed, moistened, in a thin layer to the air, whilst the other was being thus treated. Both portions were now mixed separately with equal quantities of grape-sugar, dissolved in 10 parts of water, and exposed to a temperature of 95° F. The portion containing the uninjured yeast began to ferment in half an hour,

and continued to do so until the whole of the sugar was decomposed. The mutilated yeast did not produce a single gas-bubble in the fluid containing it during the whole of this time.—Poggendorff's *Annalen*, No. iii. 1846.

ANALYTICAL CHEMISTRY.

Observations on the Method proposed by M. Levöl for the Determination of Silver. By M. GAY-LUSSAC.

AFTER having confirmed by several experiments the accuracy of M. Levöl's process*, I thought it might be simplified by adding to the nitric solution of silver the ammonia and acetic acid at one and the same time, but in sufficient quantity to saturate the whole of the nitric acid, both that in combination with the silver and that in the free state. 10 grms. of acetate of ammonia were added with a little water to the silver dissolved in 5 centimetres of nitric acid of 1.282. A considerable magma of acetate of silver immediately resulted, upon which was poured a normal measure of culinary salt. The assay being finished, the quantity indicated by synthesis was found very accurately, although, following the example of M. Levöl, I had added to the silver as much as $\frac{1.000}{1000}$ ths of mercury.

Wishing to confirm the utility of the ammonia in the process, I substituted for the acetate of ammonia acetate of soda, which I employed in crystals in the proportion of 10 grms.; the quantity of silver was again found very accurately, the chloride of silver became blue on exposure to light, and the mercury was readily detected in the supernatant liquid. It results consequently from this observation, that the theory of M. Levöl, which consists in admitting the formation of a subnitrate of ammonia and mercury, is not correct, since the ammonia may be replaced by soda. This theory fails in two respects, for the nitric acid may likewise be replaced by concentrated sulphuric acid to dissolve the silver, yet everything remains the same.

Lastly, to ascertain whether the excess of acid was not necessary to hold the mercury in solution, two samples were prepared, to which was added the normal solution of chloride of sodium, and then each chloride of silver dissolved in ammonia; but the saturation of the alkali was now effected in one of the assays with nitric acid, and in the other with acetic acid, so as to obtain a weak acid reaction, solely appreciable by blue litmus-paper. The sample continued to give an exact amount for the assay in which the neutralization had been made with acetic acid; but for that in which nitric acid had been employed there was an excess of 8 thousandths in 20 of mercury which had been employed. 12 thousandths of mercury had therefore been retained in solution, and the 20 would probably have been if the neutralization had been more accurate relatively to so small a quantity of mercury. However, without having endea-

* Described at p. 184 of the present volume.

voured, from want of sufficient time, to establish the true theory of the process, I may state, that in a practical point of view no free mineral acid must be left in the silver solution, and that it should be entirely saturated with acetate of soda.—*Ann. de Chim. et de Phys.*, June 1846.

On the Estimation of Albumen in Animal Fluids.

By J. W. GRIFFITH, M.D.

The estimation of the amount of albumen in animal fluids, as usually directed, is not one of the simplest analytical proceedings. The following modification is so simple and effective, that I have been induced to make it public.

If the fluid be alkaline, it should be neutralized with very dilute muriatic acid; if the reaction be not perfectly neutral, it should be acid rather than alkaline, but very slightly so. A portion weighed before neutralization is then rapidly boiled in a platinum crucible, over an open lamp, constantly stirring with a glass rod during the ebullition. The heat is thus diffused throughout the mass, and the albumen separates in a granular disintegrated form, which is readily collected on a filter, washed, and the formation of the ordinary gelatinous flakes is entirely prevented. It is also much more readily and perfectly dried, powdered and acted upon by the ordinary reagents. If the vessel in which the ebullition is effected be shallow, the evaporated water may be replaced during the process.

CHEMICAL PREPARATIONS.

On an Impurity occurring in Commercial Aqua Ammonia.

By DOUGLAS MACLAGAN, M.D., F.R.S.E.

SOME time ago having occasion to add nitric acid to a fluid containing an excess of ammonia, I was perplexed by observing that the liquid assumed a deep red colour passing to purple. As this was a reaction which I had not the least reason to expect in the experiment in question, I suspected impurity in the nitric acid, which had been prepared by myself as a pure reagent, and repeated the trial with the same acid and ammonia, when a similar result followed. Circumstances prevented me from inquiring further at that time into the cause of this, and it had escaped my recollection, until I called at an extensive drug warehouse here to procure some strong aqua ammonia, D. 880. I was then told that if I did not care about having it quite pure, I could have some of great saturating power, but containing some foreign matter like coal-tar, which would render it unfitted for use as a pure chemical reagent; at the same time I was told that the whole of the ammonia (of which I took a few ounces) was not equally thus contaminated. This recalled to my recollection the circumstance which had previously occurred to

myself, and I accordingly subjected this sample to the action of nitric acid, but without producing the least trace of the red coloration. I mentioned this to my friend Dr. Anderson, whose recent investigations into the volatile products of coal-tar* were likely to have directed his attention to this matter. I found that he had not observed it, but I speedily showed him the characteristic reaction on a sample of aqua ammoniæ D. 920, in his own laboratory which he had procured from the same drug-warehouse. Dr. Anderson kindly assisted me in making some experiments to determine the nature of this impurity, and a few minutes sufficed to show that the impurities here were, a considerable amount of the volatile substance called *pyrrole* discovered by Runge, and a portion of what was probably naphthaline.

The following were the experiments to which this impure aqua ammoniæ was subjected:—

1. The addition of an excess of nitric or sulphuric acid caused a rapid red coloration passing into purple.

2. The ammonia was supersaturated with muriatic acid and a clean shaving of fir-wood inserted into the fluid. It speedily became dyed of a rich purple. This is characteristic of pyrrole.

3. A portion of the ammonia was supersaturated with sulphuric acid and distilled. The distilled liquid had a marked odour of naphthaline, and crystalline-looking particles apparently of this substance floated in it. It was tested by muriatic acid and the fir-wood, and gave very strongly the colour characteristic of pyrrole. Pyrrole was considered by Runge to be a base, but it distils over even from a large excess of sulphuric acid. Hoffman, in his investigation of aniline, failed to obtain this substance previously discovered by Runge, but Dr. Anderson, in the researches quoted above, found it in abundance.

4. The residue of the distillation in the last experiment, which of course contained all the ammonia in combination with the sulphuric acid, was mixed with a small quantity of caustic potash. The smell of *picoline*, the new base recently discovered by Dr. Anderson, was distinctly perceived. More potash was then added, and the fluid distilled, when the ammonia passed over. It was now again tested for pyrrole, but hardly a trace of it could be detected.

It is easy to see how these impurities come to be present in the ammonia. It is well known that most of the ammonia of commerce is derived from the watery liquor of gas-works, from which it is prepared by converting it into sulphate or muriate, and, decomposing the salt so obtained, by lime. In the preparation of this impure aqua ammoniæ it is obvious that this process has not been followed. The manufacturer, in order to save the expense incurred by converting it into sulphate or muriate, has contented himself with procuring it by direct distillation, and thus it contains the other volatile ingredients of the gas liquor.

It is hardly necessary to say that such aqua ammonia is quite un-

* Trans. Royal Society Edinb., vol. xvi. p. 2.

fitted for chemical or pharmaceutical use. It is sold at a lower price than the ammonia of the same strength as it ordinarily occurs in commerce. That which was the subject of the above experiments, I am informed, was procured from England.

I suspected that this impure ammonia might also contain traces of hydrocyanic acid, but none could be detected by the ordinary tests.—*Monthly Journal of Medical Science for June 1846.*

Advantageous Method of preparing Gallic Acid. By F. MUELLER.

The author recommends Braconnot's method for preparing gallic acid, modified as follows. He boils 16 oz. of coarsely-pounded so-called heavy blue galls 3 times with 8 lbs. of water in a tin sauce-pan, strains the decoction, and lets it stand for 4 months in a covered earthenware pan, at a temperature of 100°–122°, now and then replacing the evaporated water and well agitating. The mould, as well as the crusts which formed, are after this time collected on a filter, slightly washed with cold water and dried, then boiled with 4 parts water, filtered, and the residue well washed with hot water. The crystals which separate from the filtered solution on cooling are separated from the mother-ley, slightly washed, dissolved in a little boiling water, and set aside to crystallize. The crystallized acid is collected on a filter, rinsed once or twice with water, dried, then digested for several days with 3 oz. of alcohol and 1 oz. of purified animal charcoal, heated to boiling, filtered, and evaporated at a very gentle heat. The still slightly brownish crystals are again collected on a filter, rinsed with spirit, dissolved in 3 parts boiling water, and set aside to crystallize. The crystals obtained were now of a beautiful white colour, silky lustre, and perfectly pure. The mother-ley yielded on evaporation a small quantity of brownish-yellow crystals. The produce in beautiful white gallic acid amounted to 2½ oz. In another experiment, 3 lbs. of galls yielded 8 oz.—*Archiv der Pharm.*, xlv. p. 153.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

May 18, 1846. (The President, Professor Graham, in the Chair.)

A highly interesting paper was read from Dr. Redtenbacher of Prague, "On the Volatile Fat Acids arising from the Oxidation of Oleic Acid by means of Nitric Acid."

In this way were obtained the acetic, metacetic, butyric, valerianic, capronic, cænanthyllic, caprylic, pelargonic and caprinic acids, comprising the whole series of fat acids boiling below 300°. The general production of these volatile fatty acids from oleic acid explains their occurrence in almost all fatty bodies. In the fat of hens, geese, snakes, the hare, and particularly human fat,

Dr. Redtenbacher has found without exception small quantities of volatile fatty acids. The most diffused appear to be the caprylic, capronic and valerianic acids. In a diluted state the caprylic acid produces on the organs of smell the same effect as the sweat of a healthy man; and it is probable that this acid is carried off with the perspiration during violent exercise.

"On the Compounds of Phosphoric Acid with Aniline," by E. C. Nicholson, Esq.

The only analysis of the phosphate of an organic base yet published is that of the phosphate of strychnine by M. Regnault, which agrees best with the formula $\text{HO}, \text{C}^{44} \text{H}^{33} \text{N}^2 \text{O}^4, 2\text{HO}, \text{PO}^5$. To contribute towards filling the void in this important division of chemical science the present researches were undertaken, the artificial base aniline being chosen. The following compounds were obtained:—

When aniline is added in excess to a strong solution of phosphoric acid, the whole instantly solidifies to a white crystalline mass of salt, which, drained and redissolved in hot water, forms beautiful flesh-coloured nacreous plates, like those of thionurate of ammonia. It is fusible by gentle heat, and readily decomposed. This salt is composed of $2(\text{HO}, \text{C}^{12} \text{H}^7 \text{N}) \text{HO}, \text{PO}^5$, and is consequently analogous to common phosphate of soda, with 2 equivs. of fixed base and 1 equiv. of water.

A phosphate of aniline, corresponding to acid phosphate of soda (biphosphate), was obtained by addition of solution of phosphoric acid to the above salt until it ceases to precipitate chloride of barium. It forms white silky needles, very soluble in æther and alcohol, but is decomposed by water with production of the common phosphate.

The author did not succeed in forming a compound containing 3 equivs. of aniline, the analogue of the subphosphate of soda.

Two compounds of aniline with pyrophosphoric acid appear to exist, only one of which however was insulated; this was the acid phosphate with 1 equiv. of base, a salt crystallizing in white needles like sulphate of quinine. It is soluble in water, but scarcely so in alcohol and æther.

Metaphosphate of aniline forms a gelatinous white mass, soluble in water, and almost insoluble in alcohol and æther. When its solution is boiled for a long time, it is converted into common phosphate of aniline.

The attempt to prepare salts, in which aniline should be associated with another fixed base, was unsuccessful.

All the compounds of aniline with the different modifications of phosphoric acid are anhydrous.

These experiments lead to the inference, that the organic bases resemble those of mineral chemistry in their relations to polybasic acids.

"On Palmic Acid," by Lyon Playfair, Ph.D.

After alluding to the experiments of Baudet, on the solidification of castor oil by nitric acid containing peroxide of nitrogen, and the consequent production of palmine and palmic acid, the author pro-

ceeds to detail his own investigations on this subject, with the view of analysing the products. The methods of preparation and purification are fully described; and the analyses lead to the following formulæ:—Palmitic acid, $C^{34} H^{52} O^5$, and when obtained by its saponification with potash, $C^{34} H^{33} O^6$, or an equivalent of water in addition; palmitine, $C^{37} H^{54} O^6$; palmitic æther, $C^{38} H^{57} O^6$, or 1 equiv. of palmitic acid and 1 of æther. The leading characters and properties of the above compounds are also given in detail.

“On Tribasic Boracic Æther,” by J. E. Bowman, Esq.

Mr. Bowman first details his method of obtaining silica in a state resembling quartz, according to Ebelmen’s directions. It then occurred to him, from the analogous properties of silicon and boron, that a boracic æther could be produced by a decomposition similar to that of the chloride of silicon. By following this process, he obtained a heavy liquid, which was deposited above the surface of the alcohol, through which it sank, and, gradually mixing, formed a clear solution. After some time the liquid became turbid, owing to the formation of minute globules of a new fluid, unmixable with the first. This new fluid was considerably lighter than the first; and the globules, as they separated, rose to the surface.

The heavy liquid appears to consist of a chlorinated compound, and gives on analysis—

46·29 C	} nearly in the proportion of alcohol.
11·86 H	
32·32 O	
9·53 Cl	

and a trace of boracic acid.

100·00

Its boiling-point is about 190° , and its specific gravity 0·901; smell, aromatic; taste, acid and pungent.

The lighter liquid gave more satisfactory results. In the fourth distillation he obtained a pure product, having a specific gravity of 0·871, and boiling-point 250° . By analysis with chromate of lead, the following results were obtained:—

C	47·69
H	9·90
BO^3	24·29
Chlorine (accidental)	0·18

It is therefore clearly a tribasic boracic æther, and the density of the vapour confirms this view.

Tribasic boracic æther is a colourless liquid, with a pungent slightly-aromatic smell and acrid taste. It fumes on exposure to moist air.

A paper was read by Dr. Kolbe, “On the Formation of Nitric Acid, as a Source of Incorrectness in the Eudiometric Analyses of Mixtures of Inflammable Gases containing Nitrogen.”

The author detailed some experiments, which confirm the views of Cavendish on the formation of nitric acid, and prove at the same time that gaseous mixtures, rich in inflammable gases and containing

comparatively little nitrogen, cannot be analysed merely by their combustion with oxygen in the eudiometer, in consequence of the nitrate of protoxide of mercury being so largely generated as to cause the result of the analysis to vary several per cent. Dr. Kolbe showed that this source of error can be obviated by mixing the gases before the combustion with a larger or smaller volume of atmospheric air. By these means a decrease of the temperature of combustion is effected to that point at which the affinity of the nitrogen for the oxygen ceases. This, as is shown by a series of experiments, is not far removed from the point at which the gases cease to be inflammable, and can in all analyses easily be found out by a short preliminary experiment.

PATENT.

Patent granted to William Maugham and Archibald Dunlop, for Improvements in the Manufacture of Ale, Porter, and other Fermented Liquors.

THIS invention consists in heating ale, porter, and other fermented liquors (after they have undergone the ordinary process of vinous fermentation), to such a temperature as to arrest the further progress of the vinous fermentation, in order that the liquors may be introduced into bottles under pressure, with the addition of carbonic acid gas.

The ale, porter, or other fermented liquor, is put into a cask, or other suitable vessel, containing a coil of tin-piping similar to the worm in a worm-tub; and the liquor is brought to a temperature of from 150° to 160° F. by passing steam through the pipe. While the heating process is going on, the bung should be inserted into the bung-hole of the cask (but only so tight as to require a slight exertion to remove it), to prevent the liquor from being exposed to the external atmosphere; and as soon as the required heat has been obtained, the cask is to be securely closed, and then the liquor is to be cooled down to the temperature of the atmosphere by passing cold water through the pipe. After the ale or porter has been thus heated and cooled down, the patentees, instead of using what are termed "finings" for rendering it clear and bright, effect this object by passing it through a filter, taking care that as little air be admitted to the liquor as possible. For this purpose, the cask or vessel containing the ale or porter is connected with the upper part of a closed filter, composed of layers of sand and animal charcoal, and the lower part of the filter is connected with the receiving vessel, which is exhausted of air, and then the ale or porter is permitted to flow from the cask, through the filter, into the receiving vessel, a sufficient quantity of air being admitted into the cask to allow this to take place. The ale or porter is then charged with carbonic acid gas and bottled.—Sealed Nov. 27, 1845.

THE CHEMICAL GAZETTE.

No. XCI.—August 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on the Blood. By M. DUMAS.

THE peculiar process, first pointed out by Berzelius and developed by Muller, enabled MM. Lecanu and Figuier to obtain the globules of the blood in a state of perfect purity. This process consists in mixing the stirred blood, from which the fibrine has been removed, with 3 or 4 times its volume of a saturated solution of sulphate of soda; the fluid in which the globules float then passes through the filter limpid and colourless, and the globules remain on the filter in a pure and perfect state. To succeed in this experiment, the blood should be freshly drawn; and when the fibrine has been coagulated after stirring, it is filtered through a fine linen cloth, and at once mixed with the sulphate of soda. In washing the globules however with the sulphatic solution, the filtered fluid soon becomes coloured, and the colour is darkened. M. Dumas has found, that as long as the globules are in contact with the air or aërated water, *i. e.* as long as they retain their arterial condition, the filtered solution is colourless; but when they have assumed a violet tint, characteristic of venous blood, the solution becomes coloured. The globules must therefore be retained in the arterial state as long as the filtering and washing are continued. M. Dumas effects this by immersing a drawn-out tube in the filter, and sending a constant and rapid current of air through the solution. This aëration renders the arterial conditions of the globules permanent. By washing thus effected, the globules may be separated from the serum. The process should be effected as rapidly as possible, and the temperature should be maintained at that of the body of the animal. These combined precautions in a few hours furnish pure globules, provided the quantity prepared does not amount to more than 75 or 90 grs.

The rapid alteration which the globules undergo when deprived of the direct contact of the air or aërated water, and the extreme rapidity with which, in a layer of the globules, those situated on the surface absorb the whole of the oxygen dissolved in the water, not allowing a solution proper for arterialization to have access to the lowermost globules, are circumstances well-deserving the attention of physiologists.

In fact, in discussions on the theory of respiration, the blood has always been regarded as a homogeneous liquid, coming into contact with the air in the lungs, and undergoing more or less rapid alterations. Undoubtedly the serum constitutes such a liquid, and I shall not discuss the part it takes in the phænomena of respiration; but the globules of the blood constitute so many vesicles floating in the serum, endowed with a peculiar respiration, the effects of which, with those which result from the respiration of the serum, together produce the general respiratory phænomena of the blood. We might, therefore, disregarding the peculiar action of the serum on the air, say that the respiration of the higher animals, especially of man, has for its special object to furnish oxygen to the globules of the blood, and to expel the products into which they convert it. Hence, if we attempt to calculate the effects of respiration, we must take into account the membranes which form the envelopes of these globules; for we know how different from pure and simple solution of gases are the remarkable phænomena of endosmose, which occur through the membranes separating two reservoirs containing different gases, or two liquids also containing dissimilar gases. The property of assuming the bright colour in arterial blood belongs to the globules; it is independent of the albumen of the serum, of the fibrine of the blood, and of the vitality of the animal. All alkaline salts do not act, as regards this property, like the sulphate of soda. The ordinary phosphate of soda which exists in the blood, like the sulphate, may be mixed with the blood to saturation, without affecting its capability of being converted into arterial blood. Blood which has been saturated with phosphate of soda, when agitated with oxygen, assumes a brighter red arterial tint than before this addition. Thus, as regards this property at least, the blood is capable of receiving much larger quantities of sulphate or phosphate of soda than it contains. The same applies to the salts of organic acids, as the potassio-tartrate of soda, which admits of the supposition that the lactate of soda may exist in the blood, even in considerable quantity, without exerting any injurious influence in this point of view. But the same does not apply to the chlorides of sodium and potassium. If fresh-beaten blood be saturated with chloride of sodium, and immediately shaken with oxygen, the colour remains violet and dark. Muriate of ammonia produces the same effect. Is there any relation between these phænomena and the opinion that the abuse of salted meats predisposes to scorbutus? Those salts, which, when present in the blood, enable it to retain its power of arterialization, are those which preserve the globules entire, and enable it to furnish a colourless serum on filtration. On the contrary, those which remove the capability of its becoming arterial, allow the more ready formation of a coloured serum. These experiments induce us to believe that the colouring matter of the blood is especially fit for assuming the characteristic tint of arterial blood, when it is combined with the globules into the composition of which it enters. This character becomes modified or lost, when the colouring matter is really dissolved, by the destruction or alteration of the globules. On care-

fully comparing specimens of the same blood, placed in contact with alkaline salts, and susceptible of saturation with these salts in the cold, it has appeared to me that in general these saline solutions, when agitated with oxygen, behave as follows:—Those salts which contain complex organic acids, as tartaric and citric acids, preserve the integrity of the globules better than the salts of mineral acids. The soda salts maintain this integrity better than potash or ammonia salts. There appears then to exist an unexpected connexion between the integrity of the globules, the arterial state of the blood, the phenomena of respiration, and the nature or the proportion of the salts dissolved in the blood. A few experiments of this kind suffice to convince one that asphyxia may be produced in the midst of air and oxygen without any change in the appearance of the phenomena of respiration, by the simple introduction of salts which modify the condition of the globules of the blood as regards oxygen.

The elementary analysis of the globules of the blood has become so simple, that I have accomplished it with perfect confidence in the results. The globules of the blood, perfectly freed from serum and dried on shallow dishes *in vacuo* over sulphuric acid, yield, in a very short time, a perfectly dry residue. When this has been treated with boiling æther and alcohol, it becomes insoluble in water, which then removes the sulphate of soda mixed with the globules. My analyses of the substance were made when it had been thus treated. After deducting the ash, it was composed of—

	Globules of the blood			
	of Woman.	of the Dog.		of the Rabbit.
Carbon	55·1	55·1	55·4	54·1
Hydrogen	7·1	7·2	7·1	7·1
Nitrogen	17·2	17·3	17·3	17·5
Oxygen, &c.	20·6	20·4	20·2	21·3
	100·0	100·0	100·0	100·0

It is evident from these analyses, as had been concluded from the properties of the blood, that these bodies belong to the family of albuminoid matters. If the carbon which they contain amounts to a per cent. more than that in albumen or caseine, it is because the colouring matter of the former is more highly carbonized than the latter.—*Comptes Rendus*, June 1, 1846.

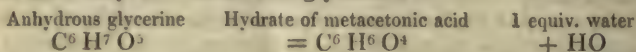
On the Presence of Copper in the Bile.

Dr. Gorup-Besanez has found, that not only the dark-coloured biliary calculi, but even the human bile, yields distinct traces of copper. Ox-bile also contains an extremely minute quantity of a metal, which forms a brown precipitate with sulphuretted hydrogen; but, on account of its minute amount, we have no proof of its nature.—Heller's *Archiv*.

On the Conversion of Glycerine by Fermentation into Metacetic Acid. By Prof. J. REDTENBACHER.

Some time ago Gottlieb described a new acid under the name of metacetic acid ($C^6 H^5 O^3 + Aq$), which he obtained by the action of fusing hydrate of potash upon starch, gum, sugar and mannite, and proved its origin from metacetone by experiment*.

Metacetic acid has great resemblance to acrylic acid $= C^6 H^3 O^3 + Aq$, from which it only differs by 2 equivs. of water and the fusibility of the silver salt; but with respect to its formula it is quite as closely connected with glycerine, for



I endeavoured therefore to obtain the one or other acid from glycerine by spontaneous decomposition.

It has frequently been attempted to set glycerine in fermentation by means of yeast, but all the experiments proved unsuccessful. I dissolved pure glycerine in a large quantity of water, mixed it with some well-washed yeast, and let it stand in an open vessel for several months at a temperature of 68° to 86° F. After some time the liquid began to exhibit an acid reaction, a faint evolution of gas took place, the yeast collected partially on the surface and began to grow mouldy. The free acid was saturated from time to time with carbonate of soda, the evaporated water replaced, and the yeast which collected on the top stirred into the liquid. As soon as the liquid acquired no further acid reaction, it was filtered and evaporated. The saline mass obtained was yellow, and possessed the smell of *sourkraut*. It was decomposed with sulphuric acid and distilled in a retort; the product was milky, very acid, had the same odour as the soda salt, only stronger, and minute drops of oil collected on the surface. It was saturated with ammonia and precipitated with a solution of silver, when it yielded an abundant white precipitate, which became somewhat black from the presence of a little formic acid. The precipitate was boiled and filtered, when small, hard, granular, white crystals of a silver salt separated from the liquid on cooling, which fused on the application of heat, and otherwise possessed all the properties of the metacetate of silver. On analysis it yielded—

Carbon.....	19.89	6 =	450.0	19.89
Hydrogen	2.70	5	62.5	2.76
Oxygen	12.78	3	300.0	13.26
Oxide of silver....	64.63	1	1450.0	64.09

It is evident therefore that metacetic acid is formed from glycerine by slow decomposition, yeast and access of air. A portion of the silver salt, which subsequently separated, had exactly the appearance and properties of the double salt of acetate and metacetate of silver described by Gottlieb, and on analysis yielded

* See Chem. Gaz., vol. iii. p. 157.

numbers corresponding to the formula $C^4 H^3 O^3 + AgO + C^6 H^5 O^3$, AgO .

The mode of procuring metacetic acid from glycerine is preferable to preparing it from metacetone. With the last method, such a large quantity of acetic acid is each time obtained, that the separation of the two acids is somewhat tedious. With respect to the properties of metacetic acid, I may add that it is indeed very soluble in water, but not in every proportion, as I obtained it floating in small oily drops on the saturated aqueous distillate.—*Liebigs Annalen*, Feb. 1846.

On the Employment of Magnesia in the Treatment of poisoning by Arsenious Acid. By A. BUSSY.

The results of my investigations are,—

1. That purified animal charcoal, recently proposed as an antidote in cases of poisoning with arsenic, cannot be employed with success for this purpose.

2. That pure but slightly calcined magnesia readily absorbs arsenious acid in solution, and forms with it a compound insoluble even in boiling water.

3. That in the gelatinous state it absorbs it still more rapidly.

4. That animals to which arsenic had been administered were constantly saved when sufficient doses of magnesia were subsequently given to them.

5. That this antidote has an advantage over all those hitherto employed, of being always on sale at every chemist's shop, that it readily and entirely neutralizes the poison, that a large amount may be administered without inconvenience, and that its general therapeutic effects are of themselves in relation with the indications to be fulfilled in such cases of poisoning.

6. That magnesia decomposes tartar-emetic, salts of copper, and corrosive sublimate; and there is reason to believe that it might be employed with success in combating and mitigating the effects of those poisonous substances, and that of metallic salts in general.

7. That the salts of the organic alkalies, morphine, strychnine, &c., being equally decomposed by magnesia, the use of this substance in cases of poisoning by organic products, whose action is owing to the presence of some vegetable alkaloid, might retard and render the absorption of the poison more difficult. This however I intend to confirm by subsequent experiments.—*Comptes Rendus*, May 18, 1846.

On the Decomposition of the Sulphocyanide of Lead and Copper by Sulphuretted Hydrogen. By ALEX. J. JAMISON.

The decomposition of the sulphocyanide of lead and copper by sulphuretted hydrogen having recently been rendered doubtful by some statements of Dr. Völkel, with which he endeavoured to sup-

port certain theoretical views, induced the author to make the following experiments.

The question as to the decomposition of the above sulphocyanides by sulphuretted hydrogen may be stated as follows:—Can one of these sulphocyanides be completely converted by sulphuretted hydrogen into a corresponding sulphuret, sulphocyanide of lead into sulphuret of lead, sulphocyanide of copper into sulphuret of copper?

To decide this, pure, recently-precipitated, moist sulphocyanide of copper was suspended in water, and sulphuretted hydrogen passed through the liquid until it was saturated. The compound immediately changes its white colour into a brown in contact with sulphuretted hydrogen. When the brown precipitate had been left during the night in the liquid, decomposition was generally quite complete, as the following analysis will show. If the supernatant water is changed once, and again saturated with sulphuretted hydrogen, complete decomposition is certain. To determine the amount of copper and sulphur, the sulphuret of copper was fused with a mixture of nitre and carbonate of soda, the oxide of copper obtained weighed, the filtered solution precipitated with chloride of barium, and the quantity of sulphur calculated from the sulphate of barytes. The precipitate consisted of—

			The composition of the sulphuret of copper is
Copper	79.68	79.763	79.762
Sulphur	20.27	20.270	20.238

The black precipitate, obtained exactly in the same manner by passing sulphuretted hydrogen into sulphocyanide of lead which had been suspended in water, yielded on analysis—

			Sulphuret of lead consists of
Sulphur.....	86.64		86.576
Lead.....	13.33		13.425

These analyses leave no doubt that the sulphocyanides in question are completely decomposed by sulphuretted hydrogen, and converted into sulphurets.—Liebig's *Annalen*, May 1846.

Remarks on the Constitution of the Human Bile.

By GEO. KEMP, M.D. Cantab., F.C.P.S.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,—Your Number for July 15th contains at page 280 an extract from Heller's 'Archiv' of some important discoveries by Dr. G. Besanez, in which an allusion is made to my researches on the human bile; and which, from some cause or other, say inadvertence, imputes to me a mode of procedure utterly inconsistent with candid research and the steady aim which I have kept in view, the ungarbled and unprejudiced statement of facts. I feel therefore convinced that you will grant me the indulgence that you recently did to Dr. Wright, of correcting the error. The following is the sentence to which I allude:—"Kemp has asserted that the composition of the

human bile is entirely different from that of the ox-bile, and has endeavoured to prove it by ultimate analysis." If Dr. Besanez will do me the favour of referring to the Transactions of the Cambridge Philosophical Society, vol. viii. part 1, he will see the account of my analyses of the human bile, stated as a simple fact, devoid of all theoretical deduction. This paper was read on the 3rd of March 1843, and nine months before the assertion to which he alludes was made. I stand therefore acquitted of the charge of having made an assertion, and then attempting to prove the truth of that assertion by analysis; nor do I feel myself less entitled to acquittal of the charge of having, without due cause and consideration, made the assertion alluded to. A difference of 4 per cent. in carbon, with a combining weight which leads to a different formula, is surely sufficient to justify my opinion: nor can the difference alluded to admit of resolution by the surmise, that it arose from the presence of cholidic acid. According to Dr. Besanez's discovery of the results of the diastatic influence of the mucus of the gall-bladder, the value and interest of which discovery no person can estimate more highly than I do myself, had the bile which I analysed undergone decomposition, cholidic acid, taurine and *ammonia* would have been the results; it would consequently have exhibited alkaline reaction on test-paper. On referring to my letter to Liebig, p. 17, it will be seen that this very point is most especially dwelt upon, and its perfect neutrality pointed out. Not only so—according to the analyses of Dumas and Demarçay, cholidic acid contains no nitrogen; consequently, if the body I analysed was identical with ox-bile, having an excess of 4 per cent. of carbon from the presence of cholidic acid, the quantity of nitrogen would have been diminished in a corresponding proportion; but the fact is, that human bile, according to my analyses, contains *more nitrogen* than ox-bile. I am well aware that the human bile is capable of undergoing the same metamorphoses as ox-bile, having produced choleic acid, cholidic acid and (by the action of caustic potash with evolution of ammonia) cholic acid. To this series Dr. Ronalds adds taurine. Now, although these are strong presumptive facts that a certain *analogy* exists between ox-bile and human bile, I cannot think that, with the fact of a difference in composition, as elicited, not by influence but actual experiment, we are justified in admitting their identity.

At the commencement of any research, without previous authority or experience to guide, and with every difficulty to encounter, it is by no means unlikely that oversights, or even errors, may creep in, and of such the true philosopher is the most indulgent critic; should such be the case with my researches on the human bile and that of carnivorous animals, it will be sufficient satisfaction and reward for me to have broken up the ground, exposed errors in high quarters, and agitated an important question.

Permit me, Sir, in conclusion, to make a remark on the recent discovery of sulphur in taurine by Prof. Redtenbacher, and his consequent deduction, that sulphur must also be present in bile. The existence of that element in ox-bile was discovered by me in the

year 1842, and the account published in Erdmann's 'Journal,' vol. xxviii. This fact ought, in fairness, to have been acknowledged. The quantity will, no doubt, soon be determined. I cannot, however, devote immediate attention to it, as I am engaged on a new mode of organic analysis, which will confine the practical error, both in carbon and hydrogen, to the second, or even with care to the third decimal; and I think it better to forgo other pursuits for so important a desideratum.

I remain, Sir,

St. John's, Isle of Man,
July 21st, 1846.

Your obedient Servant,
GEO. KEMP, M.D. Cantab., F.C.P.S.

On the Bibasic Arseniate of Ammonia and Magnesia, corresponding to the Bibasic Phosphate of the same Bases, with Remarks on its Application. By M. LEVOL.

Notwithstanding the striking analogy which the arsenical compounds exhibit with those of phosphorus, it does not appear that the existence of an arsenical combination, corresponding to the most important of the double ammonio-phosphates of magnesia, has hitherto been sought for; I allude to that which is met with among certain products of the animal organism, and is so frequently employed in chemical analysis, on account of its insolubility, for the quantitative determination of phosphoric acid.

With these considerations I thought it would be interesting to ascertain whether it might be possible to produce with arsenic acid the analogue of the phosphate above mentioned, to employ it, should it partake of its insolubility, for the estimation of arsenic acid. Such a salt does indeed exist: it is similar in every respect to the bibasic phosphate of the same bases and its formula resembles that assigned by Berzelius to the phosphate*, viz. $2\text{NH}^3, 2\text{MgO}, \text{AsO}^3 + 10\text{aq.}$

This salt is obtained in the same way as the corresponding phosphate, *i. e.* by adding a soluble ammonio-magnesian salt to the liquid containing the arsenic acid, after having previously rendered it ammoniacal; like the phosphate it does not make its appearance immediately, but only after some minutes, unless agitated; it is also deposited, in the form of very minute crystals, on the sides of the vessel, and its insolubility may likewise be compared to that of the phosphate. 1 part of arsenic acid, diluted with 56818 parts of water rendered ammoniacal, was made apparent shortly after the addition of a few drops of a concentrated solution of ammonio-sulphate of magnesia. I think it would be difficult to enumerate two salts more accurately comparable one with the other than the phosphate and arseniate in question.

I employed this new salt in a very difficult case of analysis, the quantitative separation of the arsenic and arsenious acids, the latter

* The water contains 5 times as much oxygen as the magnesia, and the ammonia is just sufficient to form a neutral salt with the phosphoric acid of the magnesian salt (Berzelius).

not yielding an insoluble double salt with ammonia and magnesia. The precipitate after collection is dried and heated to redness, taking care to avoid any reducing influence; there remains 2MgO , $\text{AsO}_5 = 55.74$ per cent. of the new salt, which represent 41.02 per cent. arsenic acid.

It is likewise very probable that, from the extreme insolubility of the compound which the double ammonio-magnesian salts are capable of forming with arsenic acid, they might be very useful as an antidote in cases of poisoning with this acid; and it is highly desirable that those physicians who have occasion should try the sulphate, nitrate, or muriate of ammonia and magnesia, as an antidote for arsenic acid.—*Comptes Rendus*, July 6, 1846.

ANALYTICAL CHEMISTRY.

On a new Method of estimating Lead. By FLORES DOMONTÉ.

AFTER several experiments with a view to discover a ready method for the estimation of lead, I have stopped at the following, which is simple, quick and accurate. It suffices, in fact, to dissolve the lead in an acid, to treat this solution with an excess of potash, and to precipitate the metal in a state of sulphuret by a solution of sulphuret of sodium of known strength. As will be seen, this process is analogous to that of M. Pelouze* for the estimation of copper by precipitation with sulphuret of sodium from its ammoniacal solution.

Preparation of the normal Solution of Sulphuret of Sodium.—M. Pelouze prepares his normal solution by dissolving the sulphuret of sodium in such a quantity of water, that about 30 cub. centim. of the liquid precipitate 1 grm. of metal.

I employ the same reagent, but weaken the solution; for the equivalent of lead being higher than that of copper, less sulphuret is required to precipitate 1 grm. of the first metal than for 1 grm. of the second. These quantities are in the inverse ratio of their equivalents, *i. e.* $1 : 3.2$. To 1 vol. of M. Pelouze's solution I add 3 vols. of water, which is very nearly in the proportions indicated. I thus obtain for assays of lead a liquid corresponding to that employed for copper, and have the advantage of using but one test-liquor for the two metals.

To graduate the sulphuret of sodium, I make an assay with pure metal; I weigh off 1 grm. of lead, which I place in a flask capable of holding from 150 to 200 cub. centim.; I add 7 to 8 grms. of commercial nitric acid, and apply a gentle heat; I dilute with a little water, when the metal is entirely dissolved, and treat the liquid with a solution of caustic potash, which displaces and redissolves the oxide of lead. The liquid is maintained at a temperature near to ebullition, and the test-liquor, which has been previously placed in a burette, gradually added. Each addition of liquid neces-

* See page 115 of the present volume.

sarily produces a black precipitate of sulphuret of lead; from time to time the liquid is boiled, when it brightens, and I observe carefully the precise point at which a drop of the reagent produces no further precipitate. I now read on my graduated tube how much liquid has been employed, say 40 cub. centim. This number will have in all assays the value of 1 grm.; as many hundreds of this number as have been employed, so many hundredths of a gramme of lead will the substance submitted to analysis contain. With a little practice the whole operation may be completed in 20 minutes, and the amount of lead ascertained to within 1 per cent. This is the widest limit of error, for frequently it has proved accurate to within a few thousandths.

Applications of the Process.—It is very seldom that the lead to be examined is in a state of purity; it is almost always accompanied with foreign metals, such as tin, antimony, arsenic, iron, copper, &c. Among commercial products, white lead and the pyrolignite of lead are the only ones, as far as I am aware, in which lead is the sole metal present. I shall now describe the peculiar precautions to be taken in these different assays. Tin, antimony and arsenic in no way interfere with the process, for these metals are not precipitated by sulphuret of sodium when a large excess of alkali is present. The insoluble oxides of tin and antimony might be separated by filtration, and also the arsenious acid, which is wholly retained by the stannic acid, as proved by the recent experiments of M. Levol. But this precaution is quite unnecessary; it is more simple to make the assay without filtering. With respect to iron, nickel and cobalt, they are not commonly met with associated with lead; nevertheless I ascertained that they do not in the least interfere with the success of the experiment. The same is the case with zinc (which is precipitated after the lead, as M. Pelouze has shown, but the sulphuret of which is white, while that of the lead is black). The presence of zinc is rather an advantage, for this change of colour of the precipitate is perhaps more readily perceived than the non-precipitation.

When copper occurs with lead the process is not less applicable, but it is somewhat more complicated. In a first experiment I determine the copper by M. Pelouze's method. I then make a synthetic assay on a mixture formed of a weight of copper equal to that which I found by experiment, and 1 grm. of lead. This assay shows by how many divisions my plumbimetric liquor ought to be diminished on examining the alloy. In fact, this number will be the difference between the results of the assay of pure lead (1 grm.) and those of the assay of 1 grm. of lead to which copper had been added. This being done I examine my alloy in the ordinary way.

Let us suppose that an alloy, in which analysis indicates 10 per cent. of copper, is under examination. To make the assay of such an alloy, a synthetic operation is made with 1 grm. of lead and 1 decigram. of copper; the ordinary operation is then made on 1 grm. of the alloy; synthesis will have shown how many divisions of the burette 1 decigram. of copper requires; this number subtracted from the total number obtained by my operation, and which represents

the sum of the two metals, will give as difference the number of divisions employed in the precipitation of the lead, and consequently the quantity of lead.

I will observe that the operation is most accurate when the copper forms at least one-tenth of the alloy. It will always be easy, knowing the quantity of copper, to add sufficient pure metal to make it one-tenth.

Bismuth, I confess, cannot be separated from lead by this method; but the same applies to nearly all analytical processes. The inconvenience is quite inconsiderable with respect to its application to the arts; in fact, the price of bismuth is a guarantee, commercially speaking, that this metal will not occur with lead; nevertheless I intend to continue my experiments, and I hope to arrive at an easy method of separating these two metals.

The examination of white leads and acetates of lead is extremely simple; it does not differ from those of pure lead, and needs no further direction. I will only state, that the application of my process to the analysis of these two commercial products will, in my opinion, be of some importance, for no substance is more adulterated.

The new method may also be applied to the examination of sulphate of lead; but it is not of much importance, for generally the native sulphuret of lead is examined both as to the lead and the silver it contains, and my method merely points out the quantity of lead. — *Comptes Rendus*, May 18, 1846.

On a new Method of distinguishing Baryta from Strontia by the Blowpipe. By EDWARD J. CHAPMAN*.

It is well known that baryta, strontia, and their respective salts, yield with most reagents very similar results. The property which they possess of forming with diluted sulphuric acid a precipitate which dissolves entirely before the blowpipe in a bead of carbonate of soda, serves to distinguish them from all other bodies. It is desirable therefore to be able to ascertain, by some simple process, of which sulphate the precipitate consists (presuming only one to be present), especially in cases where it may not be convenient to dilute the solution.

I have found the following method of distinguishing the two compounds to succeed perfectly:—A little carbonate of soda must be fused before the blowpipe in a loop of platinum wire, moistened with a drop of a dilute solution of any manganese salt, and exposed to an oxidating flame until on cooling the bead assume a greenish-blue colour. If then a portion of the compound under examination be fused into this, also before an oxidating flame, until the globule be almost saturated, it will either become on cooling of a light blue colour, approaching to that which it possessed before the addition of the compound, or it will change to a brown, dark gray, or greenish-brown colour. In the former case, the precipitate will be composed of sulphate of baryta; in the latter, of sulphate of strontia.

* Communicated by the Author.

Should the fused mass, after the addition of the precipitate, not give a very decided result, a little more of the manganese solution must be added, and the globule again exposed for a few seconds to an oxidating flame, when on cooling one of the above reactions will be developed.

The hydrate, and all the soluble salts of baryta, become green or blue when heated *per se* before the blowpipe with a drop of a dilute manganese solution. Salts of strontia, treated in a similar manner, become on cooling grayish-black or brown, sometimes with a slight tinge of green.

If the precipitate produced by sulphuric acid consist of the mixed sulphates of baryta and strontia, it will render the blue colour of the soda and manganese bead brown, gray, or brown mixed with grayish-green.

In this case the following simple method of detecting the presence of baryta may be resorted to by the blowpipe analyst:—The precipitate is to be fused in a small platinum spoon with 3 or 4 parts of chloride of calcium, and the fused mass digested in a little boiling water. A portion of the clear supernatant liquid, decanted into a test-tube, and diluted with 10 or 12 parts of pure water, is then to be tested with a few drops of a solution of chromate of potash. If baryta be present, a muddiness or precipitate will immediately be occasioned. It is perhaps needless to observe, that chromate of potash causes a precipitate only in concentrated strontia solutions, and produces no reaction in solutions of lime salts.

On a quick approximative Method of determining Copper by means of a Colorimeter. By M. JACQUELAIN.

The process which I am about to describe requires a balance capable of turning with 1 milligramme, 3 tubes, of which only one need be graduated, but all having an equal external and internal diameter and length of 5 centimetres from the bottom, a test-tube capable of holding 2 decilitres, an ordinary pipette, nitric acid, ammonia, caustic potash, carbonate of potash and distilled water. There is no need of preparing a test-liquor, nor of verifying its strength for each analysis; it merely requires the dissolving the alloy or ore, the partial filtration of the liquid, previously rendered ammoniacal and measured; and lastly, the addition of water to a known volume of the blue liquid until the tint resembles that of a normal solution inclosed in a sealed tube. The weight of the copper is directly proportional to the total volume of the solution diluted until the tints are uniform. By this new method of analysis, the weight of the copper may be ascertained to within three-thousandths. It includes all the cases to which the process of M. Pelouze is applicable*, and all the exceptions enumerated in his Memoir excepting that of cobalt. With respect to nickel, it is only when it is present in very large proportion relatively to the copper that it interferes.

I shall now briefly describe the principles on which this method

* See page 115 of the present volume.

is founded. All methods of analysis based on the use of measured quantities of reagents require solutions of known strength. What I wish to avoid is precisely the trouble which is occasioned by the preparation of a normal liquid, and determining its strength each day. I weigh off 0.5 gram. pure copper, dissolve it in weak nitric acid, add to the solution a slight excess of ammonia, and then sufficient distilled water to produce 1 litre of solution at 50° F. This temperature is obtained by immersing the vessel containing the solution in a bucket of water fresh from the well. The liquid is then filtered, and 5 cub. centim. of it conveyed into one of the tubes graduated up to 5 cub. centim., but not beyond, that being necessary only for the third. The tube is then wiped, and immediately sealed before the blowpipe, so that the blue solution must necessarily preserve its tint, as it can lose none of its elements by evaporation.

To obtain three tubes of the same thickness and same internal diameter, with the length of 5 centim. from the closed extremity, it suffices to take 3 lengths of one and the same piece of tubing, and to close each piece of tube at the extremities which corresponded previous to their separation before the blowpipe.

I will now describe the preliminary experiments, undertaken in order to ascertain the conditions relative to the preparation of the normal liquid and its stability.

5 cub. centim. of the blue cuprate of ammonia, prepared as above described on the 15th of April 1846, were compared with 5 cub. centim. of a perfectly similar solution, made on the 1st of June 1846, and their tints were found to be identical.

5 cub. centim. of the liquid of the 15th of April, compared with solutions of the same strength prepared on the same day with quantities of nitric acid and ammonia varying from 10 to 100 grms., all exhibited the same tint.

Solutions of the blue cuprate of ammonia, containing 1 gram., 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 grms. copper to the litre, and taken in volumes of 5 cub. centim., required additional volumes of water, accurately represented by 5, 10, 15, 20, 25, 30, 35, 40 and 45 cub. centim., to lighten their tint so as to render them identical with that of the normal solution.

To render the comparison of the tints more perfect and independent of the unequal sensibility of the two eyes, both tubes are placed against a sheet of fine letter-paper, and held between the eye and the diffused light, employing at the same time a plain blue glass fixed in a tube with a circular aperture of 2 millim. in diameter, to see through. This blue glass has the twofold advantage of deepening equally the tints to be compared.

Let us suppose that 2 grms. of an alloy of copper and of zinc are taken for examination. After solution in nitric acid and the addition of ammonia, I pour the whole into a graduated glass vessel capable of holding 2 decilitres; if the solution under examination is not so dark as the normal liquor, instead of making it into 2 decilitres, it is formed into a volume of 150, 100 or 50 cub. centim., so as always to require the addition of water to obtain the equality of

tints. I filter a portion of the measured liquid, for instance a volume of 200 cub. centim.; of this I take 5 cub. centim. in the graduated tube, and let fall in it 2 or 3 drops of pure ammonia, then water by degrees, taking care to agitate well before each observation. The tints being equal, I find that 25 cub. centim. of supplementary water have been required, and so ascertain the amount of copper in the alloy examined. The tints being equal, 30 cub. centim. of liquid will represent 6 times the quantity of copper contained in the 5 cub. centim. of the normal solution. We have consequently—

5 cub. centim. : 30 c. c. :: 0·0025 grm. : $x = 0·015$ grm. copper ;
and to obtain the total amount of copper, say—

5 c. c. : 200 c. c. :: 0·015 : $x = 0·6$ grm., i. e. 30 per cent. copper.

Comptes Rendus, June 8, 1846.

A ready Method of estimating Copper in Quantitative Analyses of pure Copper Solutions. By M. CASASECA.

The author's process consists in dissolving the copper compound in an acid, adding an excess of ammonia to the solution, and comparing the tints furnished by this solution with those which a known weight of pure copper yields likewise in the state of ammoniuret.—*Comptes Rendus*, June 8, 1846.

CHEMICAL PREPARATIONS.

On the Adulteration of the Valerianate of Zinc.
By MM. LAROCQUE and HURAUT.

For some time past a substance has been sold at Paris under the name of valerianate of zinc, of great beauty, and at a price defying all competition, which is nothing more than butyrate of zinc. This fraud, which we consider necessary to expose, is practised on such a vast scale, that at the present day nearly all the valerianate of zinc which occurs in commerce has nothing but the name and appearance of that salt.

The butyrate of zinc indeed resembles the valerianate to such a degree in its physical properties, that it is impossible to distinguish them. Thus it occurs, like the latter, in the form of light, shining, brilliant white, pearly needles. With respect to their chemical properties, their distinction is scarcely more easy, unless recourse be had to very complicated operations, requiring the skill of experienced chemists; for beyond their slight solubility in water and alcohol, both, on being treated with strong acids, yield a volatile fatty acid of a strong and disagreeable odour, which forms with barytes a salt soluble in water and alcohol, possessing the singular

property of rotating with rapidity on the surface of water, and which produces in neutral acetate of lead an oily precipitate, &c. Like the valerianate, the butyrate of zinc possesses a peculiar odour, which, although it differs very perceptibly, is nevertheless not so marked as to be appreciable by persons little accustomed to handle these products.

We thought these few details necessary to render intelligible what must happen, if, by impregnating the butyrate of zinc with essence of valerian, not merely its peculiar odour is entirely hidden, but it has acquired that of valerian itself; and we are strongly led to believe that the valerianate of zinc forming the subject of this note had undergone this treatment, for it is precisely owing to the odour of essence of valerian, which it disengages, that we were led to doubt its nature and submit it to examination.

The process by means of which we succeeded in detecting the fraud is excessively simple. It is founded on the different action which the valerianic and butyric acids exert on a concentrated solution of acetate of copper. The characteristic reaction is extremely simple and decisive. From experiments made by one of us it results that, whilst butyric acid immediately forms a bluish-white precipitate in a solution of acetate of copper, which renders it turbid, valerianic acid, on the contrary, produces no perceptible change; but by agitation it is converted into greenish drops of an oily appearance, which are partly deposited, partly float on the surface of the liquid, adhering to the sides of the vessel just like a fatty substance. These drops, consisting of the anhydrous valerianate of copper, persist from 5 to 20 minutes, and sometimes even more, and are then converted by hydration into a greenish-blue crystalline powder.

As these reactions are produced in a very marked manner only when the valerianic and butyric acids are pure or in a concentrated solution, it is therefore necessary to separate the acid of the salt under consideration. For that purpose 3 or 4 grms. of the valerianate are triturated with a little water, and then introduced into a tubulated retort to which a small balloon, serving as recipient, has been adapted. Subsequently twice or three times the weight of sulphuric acid, diluted with an equal portion of water, is poured upon the salt through the tubulature, the whole is agitated and then heated gently, taking care to avoid as much as possible any violent ebullition. Very soon a liquid passes into the recipient, which consists of nearly the whole of the acid of the salt employed and a little water. It is this liquid which is subsequently used to determine by the above reaction the nature of the product.

The distillation should not be carried too far, and a greater weight of the liquid than equals the quantity of valerianate employed should not be collected.

We have examined several valerianates of zinc in this way, the quality of which was suspicious, and the results which we obtained were always negatived with respect to the action peculiar to valerianic acid; each time, on the contrary, a turbidness was produced in the copper solution. We have repeated these experiments with

various specimens of valerianate of zinc, which we ourselves had prepared at different times, and the characteristic reaction of valerianic acid was constantly exhibited.

We also ascertained whether the solution of acetate of copper would allow of detecting a mixture of butyric and valerianic acids, and the experiments undertaken with this view have yielded very satisfactory results. Thus we found that a mixture of these two acids in very different proportions produced in the acetate of copper the reactions peculiar to each, but the appearances are not exactly of the same kind as when the acids are taken separately. In the latter case the reaction is well-defined and immediate; on the one hand, formation of a precipitate and turbidness of the liquid, butyric acid; on the other, production of oily drops, which adhere to the sides of the vessel, with the solution becoming less transparent, valerianic acid. In the case of a mixture, on the contrary, unless the proportion of butyric acid is very considerable relatively to that of the valerianic acid, the results are not so quickly evident. At first the valerianic acid manifests its presence by the production of oily drops, but the liquor does not become turbid; it is only after agitating with a glass rod for 2 or 3 minutes, that its surface, as well as the sides of the vessel and the valerianate of copper itself, is seen to become coated with pale blue crystalline needles of butyrate of copper, depending as to quantity on the proportion of butyric acid present. To avoid every cause of error in researches of this kind, it is necessary to employ a slight excess of the reagent, because valerianic acid displaces butyric acid from its combination with oxide of copper. This observation is important, for it will easily be conceived that the valerianic acid taking all the base to itself, it might readily happen that, in a mixture containing but a small quantity of butyric acid, this acid would remain free in the solution without producing the characteristic reaction.—*Journ. de Pharm.*, June 1846.

On the Preparation of crystallized Sulphuret of Calcium.

By Dr. E. RIEGEL.

The best process for procuring pure sulphuret of calcium is that recommended by Liebig, according to which 4 parts calcined gypsum, 1 part powdered charcoal, and $1\frac{1}{2}$ part meal, are kneaded with water to a paste, which is formed into pellets, which when perfectly dry are arranged with charcoal in alternating layers, and exposed to a red heat. On heating to redness a mixture of equal parts of hydrate of lime and sulphur, a preparation is obtained which contains a considerable quantity of sulphate of lime. On boiling 1 part hydrate of lime with $2\frac{1}{2}$ parts sulphur and 16 parts water for a length of time, the author obtained a brownish-yellow solution, from which on cooling some red acicular prisms separated. The crystals were quickly decomposed by exposure to moist air.—*Jahrb. für Prakt. Chem.*, xii. p. 104.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a new Process for the Estimation of Sugar.

By EUGENE PELIGOT.

SEVERAL saccharimetric processes have been proposed of late years. The services rendered to chemistry by the process of M. Biot is well known. Several modifications of this process have been made by MM. Clerget and Soleil. M. Barreswil has described a method* based on the property which an alkaline solution of oxide of copper possesses of not being acted on by ordinary sugar, while it is reduced by glucose, which precipitates the copper in the state of protoxide. Lastly, M. Payen has recently described, in a paper read before the *Société d'Encouragement*, a simple and practical method for determining, by a kind of instantaneous refining, the quantity of white crystallized sugar which is contained in the raw sugars of commerce.

The method which I am about to describe is based on well-known chemical properties and reactions. It is applicable to the sugars reduced to the solid state, such as the raw sugars, and likewise to saccharine fluids of whatever kind and origin; it requires no other instruments or reagents than those commonly met with in all manufactories, no other manipulations than those requisite for an alkalimetric test, an operation familiar to most persons engaged in chemical pursuits. It is founded on the essentially distinct action which the alkalies exert on the two kinds of sugar, the ordinary sugar (cane or beet-root sugar), and glucose (starch, grape, fruit, and diabetic sugar).

The ordinary sugar combines with the alkalies; it forms with the bases compounds in definite proportions, from which the sugar may be reobtained without its having undergone the least alteration. Glucose likewise combines with the alkalies; but it yields compounds the existence of which is of so short duration that it is impossible to preserve them unaltered more than a few instants. In fact, if a solution of glucose and potash be left to itself at the ordinary temperature, the quantity of free potash contained in the liquid is found to decrease each day, and finally disappears entirely, when an excess of glucose is employed. In fact, the glucose is converted into one or several acids, which colour the liquid brown, and form with the potash neutral salts.

The action which the alkalies exert slowly on glucose at the ordinary temperature is instantaneous when the solution of these bodies is heated to boiling; in a few minutes the conversion of the glucose into the above acids is complete.

The alkali which I employ for these experiments is lime. It is well known that pure water does not dissolve more than one-thousandth of its weight of lime, while sugar-water dissolves a consider-

* Chem. Gaz., vol. ii. p. 544,

able quantity, proportioned to the weight of the sugar which it contains. The compound which is formed when a solution of ordinary sugar is brought into contact with an excess of slaked lime has been pointed out by M. Soubeiran; it is represented by the formula $2C^{24}H^{11}O^{11}, 3CaO$. Thus a double equivalent of sugar, weighing 4275, combines with 1050 lime, or 3 equivalents.

In examining a raw sugar, 10 grms. of the sample are weighed off and dissolved in 75 cubic centimetres of water; to this solution, which is made in a glass or porcelain mortar, 10 grms. of slaked and sifted lime are gradually added, the whole is well triturated for 8 to 10 minutes, and the mixture brought on a filter to separate the undissolved lime, an excess of this base having been employed. It is well to return the liquor which has passed through a second time on to the filter, in order to dissolve rapidly the whole of the lime which the sugar is capable of combining with.

10 cubic centim. of the solution of saccharate of lime are now taken with a graduated pipette, diluted with 2 to 3 decilitres of water, and to this liquid a few drops of blue tincture of litmus are added, upon which it is accurately saturated with a solution of sulphuric acid of known strength. This test-liquor contains in the litre 21 grms. of pure monohydrated sulphuric acid. A litre of this liquor saturates the quantity of lime which is dissolved by 50 grms. of sugar.

The normal solution of sulphuric acid is first conveyed into the burette used for alkalimetric purposes, or into a burette graduated in cubic centimetres, each of which is divided into 10 parts. The burette is filled up to zero, and the acid liquid then poured into the alkaline solution, constantly stirring until the blue tint becomes reddish from the last drops of the test-liquor. On reading off the divisions on the burette of the quantity of normal acid required to attain this point of saturation, we have the quantity of lime, and consequently of sugar, contained in the solution of saccharate of lime. The total volume of this solution is ascertained by means of the table constructed by M. Payen for the appreciation of the volumes yielded by known weights of sugar and water.

For the ordinary raw sugars this suffices. I have found indeed that the proportion of glucose which they contain is too small to be appreciated by the second operation, which I shall presently describe; but it has sometimes happened that granulated glucose has been fraudulently introduced into the raw sugars previous to their refinement. To detect this fraud, and also to analyse the molasses and commercial sugars of inferior quality, which contain variable proportions of glucose, resulting from the partial alteration of the ordinary sugar consequent upon the processes employed in extracting or refining it—to analyse a product containing ordinary sugar and glucose, we proceed at first as above described for raw sugars. After the first assay, a portion of the alkaline liquid is poured into a flask or phial, which is heated in the water-bath to 212° for a few minutes. If the liquid contains only the saccharate of lime produced by the ordinary sugar, it is rendered turbid by heat, owing

to a very curious property this compound possesses of coagulating in the same way as albumen of egg when heated to 212° . But this turbidness disappears on the cooling of the liquid, and the latter does not acquire a deeper tint than what it possessed previous to being heated: on submitting it to a second alkalimetric assay after it has cooled, the quantities are found to be the same as before.

But if the saccharine products contain glucose, the solution heated in the water-bath acquires a brown tint; it yields a brown deposit, which does not disappear on cooling when the glucose is in large proportion; it gives off a decided odour of burnt sugar; lastly, the second alkalimetric assay shows a less quantity of lime than the first; this quantity belongs wholly to the ordinary sugar, the lime dissolved in the cold by the glucose having yielded neutral salts, on which the normal solution of sulphuric acid has no action.

In case the specimen examined consisted entirely of glucose, the first alkalimetric assay, after the saccharine liquid had been triturated in the cold with the lime, would indicate nearly the same amount of alkalinity as with ordinary sugar; the second assay, made on a portion of the liquid heated to 212° , would indicate the same quantity of lime as that which would have been dissolved by an equal volume of pure water.

This quantity is very small; a decilitre saturates 4 cubic centim. of the normal solution of sulphuric acid. Although the liquid is then coloured brown, its point of saturation is readily determined by taking care to add a little more tincture of litmus, and to stop the moment the solution, which becomes greenish, assumes a lighter tint by the addition of sulphuric acid.

The examination of saccharine liquids is effected in the manner above described; the only precaution necessary is to operate on liquors indicating from 6° to 8° on Beaumé's areometer. The juices of beet-root and of the sugar-cane occur naturally of this density. On employing more dilute solutions, there is great risk of not dissolving rapidly the whole of the lime they are capable of taking up; if they are more concentrated, they do not filter quickly. The quantity of slaked lime to be employed for these liquids should be such that its weight is nearly equal to that of the sugar presumed to exist in the product to be examined; this quantity is indicated approximatively by the specific gravity of the liquid.—*Comptes Rendus*, June 8, 1846.

On the Preparation of green Copper Colours free from Arsenic.

By L. ELSNER.

Several yellow vegetable pigments yield, with solution of sulphate of copper and the contemporaneous addition of an excess of solution of caustic potash, very beautiful green precipitates, which might certainly be used as colours. An extract of weld (*Reseda luteola*) affords a beautiful light green; quercitron, a dark green; sandalwood, a dark green; fustic, a bluish light green; gamboge, ditto; Persian berries, a beautiful dark green; turmeric and Barbary wood,

a dark green; annotto, a bright green precipitate. To obtain the most beautiful colours, the tannic acid must be previously removed from the vegetable pigments by a solution of gelatine. Without solution of potash the extracts always yield only a bluish-green colour, but in no case a beautiful green precipitate. The well-washed precipitates, dried at 68° – 86° , still retain their pure colour, but between 120° and 140° become olive-brown; they are not altered by alkalies and dried lime at the ordinary temperature, nor by ordinary daylight even after several weeks. The precipitates contained in general 72.5 oxide of copper, 16.5 water, and 11.0 pigment. If, in their preparation, alum is added at the same time as the solution of copper, and then precipitated with carbonate instead of caustic potash, several tints may be produced, almost all of which are of a deeper green than the kinds of green ultramarine hitherto described.—*Journ. für Prakt. Chem.*, xxxv. p. 377.

PATENT.

Patent granted to Arthur Smith, for Improvements in the Manufacture of Soda Ash.

THESE improvements in the manufacture of soda ash consist in the substitution of the vat-waste or residuum of the lixiviation of the black ash, in place of using fresh calcareous matter, for making the mixture of sulphate of soda, carbonaceous matter, and chalk or lime, which is subjected to decomposition in the reverberatory furnace.

The manner of carrying out this invention is to mix the vat-waste or residuum mass obtained from preceding operations of the soda manufacture in required proportions, with ground coal black, or charcoal and salt cake, or sulphate of soda, and to expose the mixture on the hearth of a reverberatory furnace to a strong heat, with due stirring and turning over, till the mixture becomes fully fused and decomposed. The said vat-waste is preferable for the purpose after it has lain some time exposed in a heap to the atmospheric influences, whereby it becomes deprived to a considerable degree of its sulphureous impregnation.

The proportion of vat-waste to be used for a certain weight of sulphate of soda and slack depends upon the proportion of calcareous matter in the waste, and can therefore be regulated for each particular heap only by trial or experiment. When it is relatively poor in calcareous matter, it must be used in a proportionately larger quantity.—Sealed Oct. 23, 1845.

THE CHEMICAL GAZETTE.

No. XCII.—August 15, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of Chelidonic Acid and its Salts. By J. U. LERCH.

CHELIDONIC acid was discovered by Probst. It occurs along with two organic bases in *Chelidonium*, in the same manner as meconic acid accompanies the alkaloids of opium. This circumstance led the author to suspect that the peculiar organic bases of certain families of plants are connected with the formation of the acids peculiar to those families even when the latter are combined with other bases, for instance lime. Moreover, chelidonic acid differs but little from meconic acid; like that, it is a tribasic acid whose bibasic salts are white, while the tribasic are yellow; like meconic acid, it is decomposed at a high temperature, above 392° , with evolution of pure carbonic acid gas, into other acids. It occurs in all parts of the plant, but only in very minute quantities, accompanied by a very considerable amount of malic acid, and a small quantity of another organic acid, probably fumaric acid, which Probst also found in *Glauadium luteum*. Citric acid could not be detected. The flowering period is the best for the preparation of the acid, as the plant then contains the largest quantity, while only traces occur in the young plant, but much malic acid. It is contained in the herb in combination with organic bases, but for the greater portion with lime (perhaps as a combination with the organic base and lime); and on precipitating the juice with a salt of lead, a compound of chelidonic acid with oxide of lead and lime is always obtained.

The mode of preparation is founded on a property of the chelidonate of lead, that of being insoluble in dilute nitric acid, in which the malate of lead readily dissolves. The juice obtained from the herb by pressure is coagulated by heat and filtered, acidified with dilute nitric acid, and precipitated with nitrate of lead. With a suitable addition of nitric acid a crystalline precipitate of the lead salt is obtained, which quickly subsides. When the quantity of nitric acid is too small, the precipitate falls in large dirty yellow flakes, and is not so readily deposited, from its still containing malate of lead. When too much nitric acid has been added, no precipitate results. The quantity of acid required to acidify the juice varies for each single portion of the herb with the quantity of acids in them. It is therefore advisable to employ little nitric acid, be-

cause in a subsequent operation, in the preparation of the lime salt, the malic acid may be readily separated. It is also necessary to be cautious in adding the nitrate of lead, as the precipitated chelidonate of lead is again dissolved by an excess of it. The salt so obtained is a combination of chelidonic acid with oxide of lead and lime; consequently the acid separated by decomposition with sulphuretted hydrogen always contains lime; it also contains a large quantity of colouring matter. If, previous to treatment with sulphuretted hydrogen, the lead precipitate is washed for some time with dilute nitric acid, it is nearly freed from lime and colouring matter, but a considerable loss is experienced; if, on the other hand, the separated acid is treated with animal charcoal, a considerable quantity is retained by the charcoal. The precipitate was therefore mixed with a tolerable quantity of water, and decomposed with sulphuretted hydrogen gas, which proceeded but very slowly, the liquid neutralized with chalk, some animal charcoal added, evaporated until a pellicle formed, filtered, and set aside to crystallize. The greater portion of the lime salt separated from the cold liquid in long, perfectly white, silky needles, and was nearly perfectly pure after one or two washings with distilled water. It is however very difficult to separate the acid from the lime salt; nevertheless, by repeated solution and crystallization of the lime salt from dilute nitric acid, an acid is obtained, which on burning leaves scarcely a trace of solid residue. But when once a pure lime salt has been obtained, it is very easy to combine the acid by double decomposition with another base, for instance ammonia or oxide of lead, from which the acid can be separated. With the lead salt however it may easily happen, when the precipitation takes place in concentrated solutions, that chelidonate of lead and lime are thrown down; it is best therefore to separate the acid from the ammonia salt. On the addition of 2 parts of moderately dilute muriatic acid to 1 part of a cold saturated solution of the ammonia salt, the acid separates completely, and the liquid forms a paste of acicular crystals; these are filtered, washed with cold water until the wash-water no longer exhibits the presence of chlorine, and recrystallized.

Chelidonic acid crystallizes on slow evaporation in tolerably long, colourless, silky needles, with 2 equivs. water; but when rapidly cooled it separates as a tissue of minute delicate needles with 1 equiv. water. It dissolves in cold, and more readily in hot water, also in alcohol; it is not much more soluble in acids than in water; it is not altered by muriatic acid; when concentrated sulphuric acid is poured over it, it likewise dissolves without change; but when warmed, the solution acquires a yellow colour, gives off some bubbles of gas, and on boiling becomes at first of a beautiful purple, subsequently of a dirty colour, and gives off sulphurous acid. Strong nitric acid has scarcely any action on chelidonic acid; moderately dilute nitric acid oxidizes it, with evolution of nitric oxide and carbonic acid gas, forming another acid. Oxalic acid does not appear to be produced in this operation. At the ordinary temperature and exposure to the air, and likewise over sulphuric acid and

at 212° , it effloresces and parts with the whole of its water of crystallization without further change. At 302° it gives off more water; at 428° – 437° it becomes soft and of a grayish-black colour, and gives off pure carbonic acid. If the residue be boiled with water and filtered from the separated black residue, a new acid crystallizes from the liquid in hard, somewhat yellowish crusts. When the chelidonic acid is heated with access of air, it burns with a slight deflagration.

Bibasic Chelidonates.—These are always formed when dilute solutions of chelidonic acid are neutralized with pure or carbonated oxides. When neutralized merely with pure oxide, it readily happens that a tribasic salt is formed, and the solution becomes yellow, especially with alkalis and alkaline earths, with the former of which the bibasic salt passes over into a tribasic one, even with a carbonate salt on boiling and when the solutions are concentrated. Most of the bibasic salts are soluble in water, and crystallize easily; they almost always contain some atoms of water of crystallization, which, except with the ammonia salt, is only expelled at 302° . By treatment with acids, they are converted into monobasic or acid salts; by treatment with ammonia or a fixed caustic alkali, into tribasic yellow salts. They derive no colour from the acid, and have a neutral reaction.

Bibasic Chelidonate of Silver is best obtained from the lime salt by double decomposition. It crystallizes in colourless silky needles, similar to the acetate of silver. It is soluble in water, ammonia and nitric acid, and is decomposed by the latter when heated; it is insoluble in alcohol. It remains unaltered at the ordinary temperature, and also at 212° , and is only decomposed at 284° – 302° with a slight explosion. The analysis of the salt, dried at 212° , gave—

Carbon	20.34	20.45	20.69	14 =	1050.0	20.64
Hydrogen	0.81	0.75	0.78	3	37.5	0.74
Oxygen	21.98	21.68	21.53	11	1100.0	21.62
Oxide of silver	56.87	57.12	57.00	2	2900.0	57.00

5087.5

The found atomic weight was 5089.0. Accordingly the salt contains 2 equivs. oxide of silver, and the acid is composed of $C^{14}H^3O^{11}$; but from the analysis of the yellow tribasic salts, it is evident that there is still 1 equiv. basic water contained in it, and the formula of the anhydrous acid is $C^{14}H^2O^{10}$.

Bibasic Chelidonate of Lime.—This occurs in the plant, and may be employed for the preparation of the other salts. By neutralizing the acid with chalk the bibasic salt is always obtained in brilliant white silky needles. It is sparingly soluble in cold, readily soluble in boiling water; the greater portion crystallizes from the hot saturated solution on cooling. It also dissolves in spirit, but not in alcohol, and has a neutral reaction. It does not effloresce in the air, and parts with its water of crystallization at 302° . It yielded on analysis—

Carbon	30.68	14 =	1050	30.44
Hydrogen	3.04	8	100	2.90
Oxygen	46.00	16	1600	46.37
Lime	20.28	2	700	20.29

The salt contains 5 equivs. water of crystallization; its formula is therefore $C^{14}H^8O^{10} + HO, 2CaO + 5aq.$

Bibasic Chelidonate of Baryta is obtained by decomposing the lime salt with a soluble salt of baryta; or by neutralizing the acid with pure baryta, it forms a white, crystalline, sparingly soluble powder, and parts with its water of crystallization at above 212° . It yielded on analysis 24.71 C, 1.25 H, and 45.15 per cent. baryta; its formula is therefore $C^{14}H^8O^{10} + HO, 2BaO + aq.$

Bibasic Chelidonate of Soda.—This salt should be prepared by neutralizing the acid or decomposing the lime salt with carbonate of soda, avoiding any large excess of the latter, and employing dilute solutions. It is easily soluble in water, and crystallizes with difficulty in a regular form. The crystals are silky needles, which slowly effloresce in the air, and contain 21.16 per cent., or 7 atoms water of crystallization, of which 15.50 per cent. could be expelled at 212° and 5.65 at 302° – 320° . The analysis of the salt, dried between 302° and 320° , yielded—

Carbon.....	35.38	14 =	1050.0	35.36
Hydrogen	1.55	3	37.5	1.26
Oxygen	36.28	11	1100.0	37.05
Soda.....	26.79	2	781.8	26.33

The formula of the salt, dried at 302° , is $C^{14}H^8O^{10} + HO, 2NaO$; that of the crystallized salt, $C^{14}H^8O^{10} + HO, 2NaO + 7aq.$

Bibasic Chelidonate of Lead was prepared by double decomposition of the lime salt with nitrate of lead. It is insoluble in water, sparingly soluble in very dilute nitric acid, but dissolves readily in salts of lead and in strong nitric acid; the latter decomposes it on the application of heat with elimination of the acid, or converts it into an acid salt. It contains water of crystallization, which is only expelled at a high temperature. Alkalies convert it into a yellow tribasic salt. On analysis it yielded—

Carbon	20.48	14 =	1050	20.64
Hydrogen	1.03	4	50	0.98
Oxygen	23.81	12	1200	23.57
Oxide of lead	54.68	2	2789	54.80

Its formula is $C^{14}H^8O^{10} + HO, 2PbO + aq.$

Bibasic Chelidonate of Ammonia.—When prepared from the lime salt with carbonate of ammonia, it separates from the concentrated solution in brilliant white silky needles. A solution left to spontaneous evaporation becomes quite thick, and finally congeals to a transparent mass. If this is placed on a filter, the mother-liquor drains from it, and there remains on the filter an ammonia salt, in crystals which have the appearance of the finest hair, and are as long as the basin in which they crystallized is broad. When dry it

looks like a matting of the finest silvery white hair. It contains water of crystallization, effloresces in the air at 212° , and can then scarcely be distinguished in appearance from sulphate of quinine. It is not decomposed in the air at 212° , but if the salt is dissolved several times and evaporated quickly, it acquires an acid reaction, which is also the case when it is exposed to a higher temperature. It melts when heated above 320° , becomes brown, and is decomposed with evolution of carbonate of ammonia. It yielded on analysis 38.37 C and 4.72 per cent. H. The formula for the salt, dried at 212° , is $C^{14}H^2O^{10} + 2NH^1O$. But in the crystalline air-dried state it contains 3 equivs. water, of which 1 equiv. is basic, which in the present instance escapes already at 212° .

[To be continued.]

On Vegetable Mucilage. By G. J. MULDER.

The author formerly advanced the formula $C^{24}H^{16}O^{20}$ for vegetable mucilage; two years ago, however, Schmidt detected 1 per cent. more water in it, according to which it would range with the amylum group, while the author identified it with pectine. An important circumstance in Schmidt's investigation was, that he always arrived at the same results as Mulder when he adopted the same method; the author, moreover, analysed the lead salt; Schmidt, on the contrary, the free mucilage, which is decidedly preferable, as it is doubtful whether the lead salt is pure, even when it has been freed from malate of lead. Schmidt exhausted the cold aqueous solution of the mucilage with alcohol and a dilute acid, in order to extract the insoluble salts, dissolved the pressed mucilage in water, precipitated again with muriatic acid and alcohol, washed it with alcohol, and then dried the mucilage in layers upon glass. Mulder considers the drying upon glass as unnecessary, since the mucilage forms a fine powder after digestion with alcohol; but he is of opinion that the substance so obtained is still not perfectly free from albumen and other admixtures. With the lead compound the author found very different relations, as—

	Quince.	Linseed.	Althæa.	Symphytum.	Salep.	Tragacanth.
Mucilage. . .	42.17	40.23	42.6	36.98	44.49	39.6
Oxide of lead	57.83	59.77	57.4	63.02	55.51	60.4

Schmidt's analyses nevertheless agree well, although the material was not always dried at the same temperature, but between 212° and 248° ; and Schmidt himself states that the substances examined by him were not always perfectly dry at 212° to 248° . More water might always be expelled at a higher temperature. Now since Schmidt constantly found the same quantity of hydrogen, mucilage dried between 212° and 248° should lose nothing further. To ascertain this, the author dried mucilage, prepared in the manner above described, at first for several hours in the water-bath, and then each time half an hour in a current of air of higher temperature, until no further loss in weight occurred. Quince-mucilage lost

at 212° 0.950 per cent., and between 212° and 302° , the highest temperature to which it can be exposed without decomposition, only 0.63 per cent.; while Schmidt found, between 212° and 347° , 4.96 per cent. Linseed-mucilage, dried in the same way between 212° and 347° , lost 2.31; but, according to Schmidt, 5.0 per cent.; tragacanth-mucilage likewise lost much less water than Schmidt found. Mulder hence concludes that Schmidt did not sufficiently dry his substances, as they were still capable of parting with so much water, and therefore undertook a new analysis. Tragacanth-mucilage, leaving no ash and dried at 266° , gave according to him—

	I.	II.	Equiv.	Calcul.	Schmidt at 230° .	
Carbon....	45.99	45.86	24	46.14	45.33	45.10
Hydrogen..	5.86	5.84	19	5.98	6.16	6.27
Oxygen ..	48.15	48.30	19	47.88	48.51	48.63

The formula for mucilage, is accordingly neither $C^{24}H^{16}O^{30}$, as the author had previously asserted, nor $C^{24}H^{20}O^{20}$, but $C^{24}H^{19}O^{19}$. Quince-mucilage, dried at 266° , yielded—

			Schmidt at 212° .	
Carbon	46.44	46.20	45.04	45.30
Hydrogen	6.18	6.03	6.15	6.22
Oxygen	47.38	47.77	48.81	48.48

Linseed-mucilage, dried at 302° , gave—

			Schmidt at 230° .	
Carbon	45.82	44.77	44.97	
Hydrogen	5.92	6.21	6.26	
Oxygen	48.26	49.02	48.77	

The tragacanth and linseed-mucilage still contain foreign admixtures, which cause a slight difference in the composition, although there cannot be the least doubt respecting the formula for mucilage. *Journ. für Prakt. Chem.*, xxxvii. p. 334.

On the Subnitrate of Copper. By C. GERHARDT.

Some time ago Prof. Graham advanced a theory of the subsalts, founded principally on the composition of the subnitrate of copper. This salt contains, according to the celebrated English chemist, $HO, NO^3, 3CuO$, the neutral salt being $CuO, NO^3, 3HO$. Prof. Graham states, that in the subsalt the 3 equivs. of oxide of copper replace the 3 equivs. of constitutional (not basic) water contained in the dried neutral nitrate*.

Being engaged in some experiments on the nitrates, I was incidentally led to examine the composition of the salt on which that chemist had based his speculations, and great was my surprise at finding that its composition was by no means that which he attributes to it.

The subnitrate of copper is always obtained of the same composition, whether prepared by decomposing the crystallized nitrate by

* Elements of Chemistry, 1842, p. 169.

heat or by precipitating that salt with ammonia, employed in excess or in insufficient quantity. Prof. Graham's formula supposes that the salt yields on analysis 65.5 per cent. oxide of copper and 4.9 per cent. water. The oxide of copper was determined only in a single experiment. The following are the analyses which I have made:—

I. 0.647 grm. of subnitrate, dried at 212° , and obtained by fusing the crystallized nitrate, yielded 0.428 oxide of copper.

II. 0.480 of another preparation, likewise by fusion, but dried at 482° , yielded 0.318 oxide of copper.

III. 0.621 grm. of a third preparation, decomposed with metallic copper, yielded 0.075 water.

IV. 0.863 grm., precipitated by an insufficient quantity of ammonia and dried at 482° , gave 0.573 oxide of copper.

V. 0.388 of the preceding salt, dried only at 212° , yielded 0.257.

VI. 1.037 grm., precipitated with an excess of ammonia, so that a part of the salt was redissolved, and dried at 212° , yielded 0.687 oxide of copper.

VII. 1.749 of a salt, prepared by precipitation and dried at 212° , yielded 0.213 water.

VIII. 1.1595 of another salt, prepared by fusing the crystallized nitrate, and dried at 302° , yielded 0.138 water.

According to these analyses, the composition of the subnitrate of copper is—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Oxide of copper	66.1	66.2	..	66.2	66.2	66.2		
Water	..	..	11.8	..	..	..	12.0	12.1

These results prove that the subnitrate of copper does not possess the composition assigned to it by Prof. Graham. Its true formula is $\text{NO}^{\text{b}}, 4\text{CuO}, 3\text{HO}$. Consequently Prof. Graham's theory is not confirmed by experiment.—*Comptes Rendus*, June 8, 1846.

On the Incandescence of Iron Wire in the Vapour of Alcohol.

By Dr. H. REINSCH.

The author denies the statement of Böttger*, that the incandescence of metallic wires in alcoholic vapour is attributable to the oxides already formed, as in many experiments the spiral wires continued to glow for a quarter of an hour before any oxide was perceptible. With copper not a trace of oxidation can be observed at the commencement of the incandescence, any more than with platinum and palladium. To be further convinced that the incandescence did not arise from the peroxide of iron, the author made the following experiment:—He wound some asbestos round the wick saturated with alcohol, set light to it, and let it burn until the asbestos was completely red-hot. On blowing out the flame, the asbestos ceased immediately to glow. Another piece of asbestos was now dipped into a solution of chloride of platinum, heated to redness, and wound round a wick moistened with spirit. This asbestos glowed, after it had been set light to, as brilliantly as platinum wire, so that it could not be extinguished even by the strongest blowing. Another fila-

* See page 152 of the present volume.

ment of asbestos was immersed in a concentrated solution of peracetate of iron, then heated to redness, and treated as above; but it could not be kept in a state of incandescence even after it had been heated to redness 5 or 6 times. Upon this the same piece of asbestos was wound round a carbonized wick and set light to. Where the filaments were in contact with the coal the iron was reduced, and it continued to glow at these places, although very faintly. Another piece of asbestos, treated in a similar manner with peracetate of iron, was heated to redness in a tube, hydrogen gas being at the same time passed over it. This filament, moistened with absolute alcohol and wound round the wick, glowed immediately and almost as well as the filament which had been treated with platinum. If the filament of asbestos be moistened with solutions of chloride of gold or nitrate of silver and heated, they glow almost as well as platinized filaments of asbestos.—*Jahrb. für Prakt. Pharm.*, xii. p. 91.

Observations on Magnesia as an Antidote to Arsenic.

By Dr. CHRISTISON.

Dr. Christison's attention was lately turned to this subject by a case of poisoning with arsenic having come under his notice, in which magnesia seemed to prove very serviceable. Immediately afterwards he observed it announced in a French scientific newspaper, 'L'Institut,' May 20, that a paper had been read before the French Institute two days before by M. Bussy, to prove, "That magnesia, not strongly calcined, removes arsenic entirely from a state of solution in water; that this is effected still more completely by magnesia in the gelatinous state; and that animals which have taken arsenic are invariably saved if made to swallow magnesia." While waiting for the details of M. Bussy's inquiries*, Dr. Christison made a few experiments to ascertain the amount of the action of magnesia; and he found that the dense magnesia of the shops exerts very little action in removing arsenic from solution in water; that a very light magnesia, now largely manufactured at Belfast, and quite free of carbonic acid, will remove about a twenty-fifth of its weight of arsenic from solution in water, when agitated with the solution for a few minutes; so that even ammoniacal nitrate of silver does not any longer indicate the presence of arsenic; that the same magnesia will remove about a twelfth of its weight of arsenic if agitated occasionally for a period of 8 or 12 hours; that this proportion is removed entirely in less than 3 minutes if the mixture of magnesia and water be previously near the temperature of 212° ; and that the same proportion is removed with as much speed at ordinary temperatures, if the magnesia be used in the form of gelatinous pulp, as thrown down in a cold solution of sulphate of magnesia by solution of caustic potash, and washed with cold water.

It is well known that magnesia was proposed many years ago by Mr. Hume of London as an antidote for arsenic, and that several

* The results of M. Bussy's investigations will be found at p. 293.—*Ed. Chem. Gaz.*

cases have been published in which it appeared to have been of service; but that its general utility has been doubted or denied on account of the apparent want of chemical action between oxide of arsenic and magnesia. M. Bussy's inquiries will probably clear up these difficulties. Meanwhile it appears probable, from the experiments described above, that the general belief in the want of action between magnesia and oxide of arsenic has arisen from the circumstance that for a long time no other magnesia has been in current use in medical practice in Britain except the dense variety, which appears to exert very little action on arsenic in solution on account of its great density.

Dr. Christison promises more accurate experiments and a statement of the successful case hereafter. Meanwhile it appears advisable that, when magnesia is used as an antidote, and cannot be promptly obtained in the gelatinous state, the light calcined magnesia should alone be employed, and in the proportion of between 30 and 50 parts to 1 of arsenic.—*Monthly Journ. of Med. Science*, August 1846.

On the Chromate of the Oxide of Chromium. By C. RAMMELSBERG.

When a solution of chrome alum is mixed with one of neutral chromate of potash, the first portions give rise to a brownish-red colouring, and subsequently a brilliant brown precipitate is formed, above which is an intensely yellow-coloured liquid. The precipitate may be edulcorated with cold water till the latter passes off colourless. This compound dissolves in hydrochloric acid with a yellowish-green colour, from which ammonia throws down oxide of chromium, and leaves chromic acid in solution. With nitric acid it yields a brown solution, which exhibits the same behaviour towards ammonia. Dilute sulphuric acid dissolves it slowly on boiling with a brown colour; it is readily decomposed into oxide of chromium on digestion with caustic potash; ammonia does not act upon it.

For analysis, 0.81 grm. of the air-dried substance, which lost but very little in weight up to 212° , was heated in the drying apparatus to 284° , when it gave off $0.066 = 8.15$ per cent. water. Of the substance thus dried, 0.735 grm. was heated to redness in a small retort, to which a chloride of calcium tube was adapted, and lost in this way 0.098 water, leaving a green residue amounting to 0.604, which on ignition in a platinum crucible was reduced to 0.584, and then behaved like pure oxide of chromium. The compound contains therefore—

Water	20.50
Oxide of chromium.....	74.07
Oxygen	5.03

We have here 8 atoms of chromium to 15 of oxygen, which might lead to the supposition that this body was a hydrate of CrO^2 ; such however is not the case, as the formula $\text{CrO}^2 + \text{HO}$, the only probable one, requires 17.55 water, 74.65 oxide of chromium, and 7.80 oxygen.—Poggendorff's *Annalen*, No. VI. 1846.

On the Formation of Hypo-iodous Acid, and the Reactions which occur in the Metamorphoses of this Acid. By Prof. KÆNE.

Hypo-iodous acid is not formed under the same circumstances as hypochlorous acid, since iodine has a far greater tendency than chlorine to form iodic acid. When, for instance, iodine is brought into contact with peroxide of mercury at the ordinary temperature, iodide of mercury is formed and iodate of mercury; but on heating the mixture, only iodide of mercury is produced and oxygen gas liberated. When peroxide of mercury, prepared in the moist way, is shaken with an alcoholic solution of iodine, the liquid becomes quite pale yellow; if it be filtered through peroxide of mercury into a solution of starch, this at first becomes of a meal colour, subsequently purple, and at last violet. The author shook an alcoholic solution of iodine for a few seconds with peroxide of mercury prepared in the moist way, and poured the liquid on a funnel stopped with a little asbestos; the liquid which passed very soon became turbid, and in the course of 24 hours had deposited an amorphous white powder, which is insoluble in alcohol, sparingly soluble in water, and insoluble in ammonia; concentrated nitric acid acts on it only at an elevated temperature, which is also the case with sulphuric acid. A solution of potash in alcohol precipitates peroxide of mercury from it without becoming coloured; hydrochloric acid dissolves it with evolution of chlorine, forming chloride of mercury and chlorioudous acid. Below 500° the compound remains unaltered; but when heated more strongly, it parts with water, oxygen and iodine, and is converted into iodate of mercury, and this at a temperature of above 572° into iodide of mercury and oxygen. The salt contained 29.16 per cent. peroxide of mercury; its theoretical composition is therefore 30.07 per cent. HgO , 68.70 IO^5 , and 1.23 HO , leading to the formula $2(\text{HgO}, \text{IO}^5) + \text{HO}, \text{IO}^5$. The iodate of mercury is therefore not soluble in water, as stated by Thenard. Perchloride of mercury is not precipitated by iodate of potash, but the nitrate of mercury is. The author explains the formation of the iodate in the usual way, $2\text{I} + \text{HgO} = \text{IO} + \text{HgI}$, and further, $5\text{IO} = \text{IO}^5 + 4\text{I}$.—Poggendorff's *Annalen*, lxi. p. 302.

On the Nature of the Acids contained in Tobacco. By E. GOUPIÉ.

The accuracy of the experiments of Vauquelin on tobacco having been recently questioned, I have been induced by M. Fremy to re-investigate the subject, and the following are the results at which I have arrived:—

1. Malic acid exists in tobacco, as stated by Vauquelin, for perfectly pure bimalate of ammonia may be obtained from it by the following process:—The juice of tobacco is treated with an excess of neutral acetate of lead, the precipitate washed with care, and decomposed with sulphuric acid; one-half the liquor is saturated with ammonia after having removed the sulphate of lead by filtration, then united with the other half, and evaporated to a syrupy con-

sistence; in the course of 24 hours some crystals are deposited, which are purified with animal charcoal and recrystallization. With bimalate thus obtained I have repeated all the experiments described by M. Pelouze in his memoir on the distillation of malic acid.

2. From tobaccoes grown in the south of France (Department Lot and Lot et Garonne), dried at 212° , it is easy to obtain from 3.5 to 4 per cent. in weight of bimalate of ammonia; and it would therefore be worth while to procure from this plant malic acid and the malates, the price of which is at present very high.

3. In examining the different malates, I noticed a remarkable fact with the malate of lead. It is said that this salt, when left to itself, after precipitation becomes converted, in the course of a few hours, into radiately-grouped crystalline needles; this is only true with an acid malate; if a neutral malate be employed, the precipitate does not crystallize even after several weeks; and if a few drops of acetic or nitric acid are added to it, crystallization commences after a few hours. The acid medium appears to act in this circumstance as a solvent which facilitates the crystallization.

4. Tobacco contains, besides malic acid, a small quantity of citric acid; on treating the juice of tobacco, or rather the mother-waters which have yielded the bimalate of ammonia, with acetate of lead, and decomposing the precipitate with sulphuretted hydrogen, a liquid is obtained which affords crystals of citric acid. This preparation is tedious; the crystallization requires much time, owing to the presence of deliquescent acids, such as malic and phosphoric acids, and a small quantity of lime. I judged it to be citric acid, from the appearance of the crystals, and from its yielding aconitic acid; moreover, an analysis made by M. Fremy yielded nearly the same numbers as those required by theory for the citrate of lead:—

	Found.	Theory.
Oxide of lead	67.00	67.70
Carbon	14.40	13.18
Hydrogen	1.00	1.22
Oxygen	17.60	17.90

Notwithstanding the great care with which I have repeated all the experiments recently made on tobacco, I have not been able to obtain any other than the malic and citric acids; and I feel convinced that it contains no other organic acid capable of yielding an insoluble precipitate with lead.—*Comptes Rendus*, July 6, 1846.

On an advantageous Method of decomposing Osmium-Iridium.

By J. FRITZSCHE.

As the method of decomposing osmium-iridium, by mixing it with common salt and heating it to redness in a current of chlorine, is very tedious and difficult, the author proposes the following process:—Equal portions of caustic potash and chlorate of potash are melted together in a very spacious porcelain crucible over a spirit-lamp, and into the fused mass is conveyed about 3 times its weight

of osmium-iridium, without first reducing it to powder. As soon as, on further heating, the chlorate of potash liberates oxygen, the fused mass begins to act on the osmium-iridium. The mass froths violently, so that the heat must be moderated, when it becomes more tenacious; the action at last proceeds without any further heating, the mass becomes nearly black, and the operation is discontinued as soon as the frothing has ceased. During the whole time not a trace of osmium vapours is perceptible, but a slight evolution commences on the solidification of the mass, which is increased by further heating; this however is unnecessary, so that there is scarcely any trouble with the vapours of osmic acid. 600 grms. of osmium-iridium may be fused with ease in a porcelain crucible capable of holding 2 lbs., with 100 grms. caustic potash and chlorate of potash, over a spirit-lamp; the operation lasts scarcely half an hour, and at least 50 grms. are decomposed. On treating the fused mass with water, an orange-coloured solution, containing osmium and ruthenium, is obtained, and a blackish-blue precipitate, which may very easily be separated by suspension from the undecomposed osmium-iridium.—*Journ. f. Prakt. Chem.*, xxxvii. p. 483.

CHEMICAL PREPARATIONS.

On a new Process for obtaining Formic Acid, and on the Preparation of Aldehyde and Acetic Acid by the Use of the Bichromate of Potash. By Prof. W. B. ROGERS and R. E. ROGERS.

I. Process for Formic Acid.

SINCE the important discovery of Döbereiner, that formic acid is evolved from a mixture of tartaric acid, peroxide of manganese and sulphuric acid, the progress of research has shown that in a large proportion of cases, where organic matters are exposed to powerful oxidating agencies, this acid is among the products developed; and hence several other processes have been devised for its preparation on the large scale and in the laboratory. Of these the one generally in use consists, as is well known, in distilling a mixture, in prescribed proportions, of peroxide of manganese, dilute sulphuric acid and starch or sugar.

The inconsiderable amount of acid yielded by this process, and its usually large admixture with other products, especially sulphurous acid, suggested to us, some time ago, the trial of bichromate of potash as a substitute for peroxide of manganese, and has since led us to a method of operating which we think presents decided advantages over that in general use.

When bichromate of potash, dilute sulphuric acid and sugar are mingled in proper proportions and in a proper order, a large amount of formic acid is developed, of which part passes off during the first violent reaction, and the remainder is separable by gentle distillation. Repeated experiments have convinced us that by mingling all the materials at once, before placing them in the retort, a com-

paratively small product is obtained, partly from its being volatilized by the high temperature attending the reaction, and partly, we think, because more of the sugar is carried to its highest state of oxidation in the forms of carbonic acid and water. We have therefore been led to another, and we believe better mode of operating, of which the following details will serve as an example.

Introducing into a retort, capable of holding about 1 quart, 800 grs. of bichromate of potash and 10 cubic inches of water, we gently heat the mixture so as to dissolve the larger part of the bichromate. We then add 300 grs. of powdered white sugar, and adjusting to the tubulure a perforated cork and pipette with gum-elastic bag for the gradual introduction of sulphuric acid, we slowly inject about 1 cubic inch of the latter upon the mixture. By regulating the addition of the acid and occasionally intermitting the slender stream, the violent reaction which ensues is prevented from occasioning any very great intumescence. During this stage of the operation, upwards of 2 cubic inches of a clear but feebly acid liquid passes over into the receiver. When the action has in a good measure subsided, we add 5 cubic inches more of water, and apply a gentle lamp heat, continuing the addition of the acid, by allowing it simply to drop from the pipette, until another cubic inch has been introduced. The liquid which now passes over is much stronger in formic acid than in the preceding stage, and the distillation may, without impairing the purity of the product, be continued until about 7 cubic inches have been received. By urging it much beyond this point sulphurous acid will be evolved.

100 grs. of the liquid thus obtained is capable of saturating about 7 grs. of dry carbonate of soda. Its purity is such as to fit it for immediate use in illustrating the striking reactions of formic acid and the formiates. Thus—

1. On adding a small portion of it to a solution of nitrate of silver previously curdled by ammonia, and applying heat, the silver is promptly reduced with a lively effervescence of carbonic acid.

2. With a solution of bichloride of mercury, aided by heat, it causes a precipitation of calomel and the evolution of hydrochloric and carbonic acids.

3. Combined with soda it forms a white salt readily carbonized by heat and passing into carbonate.

4. It is not blackened by sulphuric acid, but the soda salt acted upon by this acid evolves carbonic oxide with brisk effervescence.

5. This salt, heated with solution of nitrate of silver or nitrate of mercury, precipitates the metal with evolution of carbonic acid.

All these results are so prompt and striking, as to evince but little contamination of the formic acid with other products.

On comparing this process with that commonly employed, we are convinced of its superiority,—1st, on account of the exemption of the product from SO_2 , and in a great degree from other impurities; 2nd, from the much larger amount of formic acid obtained by it from an equal weight of the oxidizing material, sulphuric acid and starch or sugar; and 3rd, from the ease with which the action is controlled.

According to Liebig (Chem. Org., p. 567), 10 parts of starch, 37 parts of peroxide of manganese and 30 parts of sulphuric acid, yield 3.35 parts of an acid liquid, of which 100 grs. saturate 15 grs. of carbonate of soda. This corresponds to 7.18 parts of liquid such as we obtain. We have thus by the old process 7.18 parts of liquid of equal acidity with our product, while the aggregate weight of the starch, sulphuric acid and peroxide of manganese is 77. By our process we have about 1800 grs. of a similar acid from 2100 grs. of sugar, bichromate of potash and sulphuric acid. In other words, *by the new process we procure about 9 times as much formic acid from the same weight of the three reacting materials as by that hitherto in use.*

II. *On the Preparation of Aldehyde and Acetic Acid by the Use of the Bichromate of Potash.*

In the process described by Liebig (Chem. Org., p. 378), and which is the one hitherto generally used for preparing aldehyde in the regular way, the product is obtained from the reaction of peroxide of manganese and sulphuric acid upon dilute alcohol. This operation furnishes a liquid which is so weak in aldehyde, and so mixed with water and formic æther, and as we have found with acetic acid also, as to present the characteristic reactions only in a feeble degree, and to require two rectifications over chloride of calcium, before it can be used in forming the subacetylite or aldehyde of ammonia.

In the course of some experiments upon the reactions of bichromate of potash and sulphuric acid upon alcohol, we have been led to a process which affords a larger and much purer product, and which is entirely under the control of the operator. The distinctive features of this method are the substitution of bichromate of potash for the peroxide of manganese, and the peculiar mode of bringing the reacting materials together. In the use of the bichromate we have since found that we were anticipated by Prof. Kane, who, at page 922 of his 'Elements of Chemistry,' recommends it as a means of obtaining a purer product, and specifies briefly the manner in which he conducted the process. As however his method is not noticed in other chemical works, and as our mode of proceeding, and some of the results we have obtained, are, we think, not without novelty and interest, we deem them worthy of a brief notice in your Journal.

When alcohol is added to a strong aqueous solution of chromic acid in a retort, a very brisk reaction ensues, and upon applying a gentle heat there passes over a clear liquid, containing a considerable amount of aldehyde, with a faint trace of acetic and probably formic acids. The presence of the aldehyde is readily shown by adding a few drops of the liquid to a solution of nitrate of silver previously curdled by ammonia, and then gently heating the mixture. The oxide is speedily reduced, forming a brilliant metallic coating on the sides of the glass.

Substituting for the chromic acid of this experiment a mixture of bichromate of potash and sulphuric acid, and blending with this a

quantity of common alcohol, the reaction is extremely violent, a large volume of carbonic acid is evolved, and the liquid which distils over contains, with other products, *much aldehyde and acetic acid*. To obtain either of these substances but little mingled with the rest, special attention must be paid to the proportions in which the bichromate, sulphuric acid and alcohol are mixed, and to the order in which they are brought together. Thus, in all our experiments, we found that when *alcohol* is added *in small quantities at a time* to a mixture of the bichromate and sulphuric acid, the distilled product is almost *pure acetic acid*; but when *sulphuric acid* is *slowly dropped* into a mixture of the salt and alcohol, the liquid which passes over contains little else than *aldehyde*.

This remarkable difference in the products is, we think, readily explained by the different intensity of the oxidating power in the two cases. In the former, the alcohol, as it falls into the mixture of bichromate and sulphuric acid, being surrounded on all sides by free chromic acid, is carried rapidly through the lower stages of oxidation, corresponding to aldehyde and aldehydic acid, until by the addition in all of 4 equivs. of oxygen, and the elimination of 2 equivs. of water, it is converted into acetic acid. In the latter case, the sulphuric acid, dropping slowly into the mixture of alcohol and bichromate, liberates but a small quantity of chromic acid at any one time, and thus limits the oxidation of the alcohol in great part to the first stage, or that of the formation of aldehyde.

From the observation of these facts we were led, after a number of comparative trials, to the following process for the preparation of aldehyde.

Equal weights of powdered bichromate of potash and alcohol, spec. grav. 0.842, being placed in a capacious retort, connected with a receiver and the usual means of refrigeration, we adapt to the tubulure a pipette, charged with sulphuric acid, and whose stem reaches nearly to the surface of the liquid, the top of the pipette being furnished with a strong gum-elastic bag for injecting the acid into the mixture beneath. We now slowly add the acid, taking care to avoid excessive reaction, by sometimes allowing it merely to drop spontaneously from the pipette, and again when the action subsides accelerating its flow by pressure. At this period of the operation, the heat evolved in the retort is sufficient to carry over into the receiver a considerable volume of the aldehydic liquid; and as much carbonic acid is at the same time disengaged, the tubulure of the receiver should only be loosely closed. Having thus added gradually a weight of sulphuric acid equal to about $1\frac{1}{2}$ time that of the bichromate, we apply a gentle lamp heat, and continue the distillation as long as the aldehydic liquid passes over. When the reaction is most energetic, white fumes are evolved, which, falling from the beak of the retort into the receiver, are so dense that they may readily be poured from the latter through a funnel into a narrow-necked bottle. These, when condensed, form a clear liquid consisting chiefly of aldehyde.

By this process 1500 grs. of bichromate of potash and the same amount of alcohol have on repeated occasions yielded about 8 cubic

inches of a clear liquid, containing but slight traces of acetic acid or other extraneous matters, and possessing all the characters of a nearly pure mixture of aldehyde and water.

The product thus obtained is sufficiently rich in aldehyde to exhibit instantly and strikingly all the characteristic reactions of that substance. It may therefore, without rectification, be employed in class-room experiments and in testing for silver.

A few drops of this liquid, added in a test-tube to a solution of nitrate of silver previously curdled by ammonia, quickly converts the oxide into metallic silver, which attaches itself as a brilliant coating to the glass. In describing this characteristic property of aldehyde, Liebig and others appear to regard the *application of heat* to the mixture as necessary to the effect (*Chem. Org.*, p. 377). We have found however that the aldehydic liquid of the above process, as well as the more concentrated aldehyde procured from it by distillation over chloride of calcium, causes a complete and brilliant reduction of the oxide of silver in a few seconds *at ordinary temperature*, and that the same effect results even *when the tube is immersed in snow*, but in this case the change requires 2 or 3 minutes for its completion.

Heated with hydrate of potash, the liquid becomes yellow, then of a deep reddish-brown colour, and in a little while yields floating flakes of the characteristic *resin of aldehyde*.

On adding to the liquid an excess of caustic baryta in the cold, little or no action is manifested; but as soon as heat is applied, the mixture assumes an intense opaque yellow colour like that of chromate of lead, which by continuing the heat passes into a deep rich brown, as in the preceding experiment.

The proportion of aldehyde in the liquid as it comes from the receiver in the above process is such, that to prepare *aldehydite of ammonia* we may dispense with the two successive distillations from the chloride of lime directed by Liebig, and use the fresh product at once for this purpose. We therefore add to the liquid about half its bulk of sulphuric aether, and pass a stream of ammonia into the mixture. As the aldehyde becomes saturated, the compound in question falls in an abundant deposit of brilliant transparent rhombohedral crystals. From this, as is well known, perfectly pure aldehyde is prepared by the reaction of dilute sulphuric acid.

In some experiments, made to determine the delicacy of aldehyde as a test for oxide of silver, we obtained the following results:—

1. A solution of 1 part of nitrate of silver in 1000 of distilled water, when heated gently in a test-tube with a drop or two of aldehydite of ammonia, formed a brilliant metallic pellicle on the inner surface of the glass.

2. A solution containing 1 part in 2000 produced the pellicle in distinct spots, and not continuous as in the former case. At the same time the liquid became of a deep greenish-purple colour, and, although only one quarter of an inch thick, was nearly opaque.

3. A solution of 1 part in 10,000 gave no adherent pellicle, but on continuing the heat for 2 or 3 minutes became strongly coloured,

presenting a deep greenish-purple by transmitted, and a dull olive by reflected light.

4. In a solution of 1 part in 20,000, the peculiar greenish-purple tint was still quite decided; and even when the solution was diluted so as to contain only $\frac{1}{10000}$ th of nitrate of silver, this colour was very distinctly manifested after heating it some time with aldehydite. Compared with the faint opalescence caused by the addition of chloride of sodium to the same solution, this effect of the aldehyde appeared to be the more striking of the two.

The peculiar purplish tint of the liquid, remarked in these experiments, is evidently due to the finely-divided metallic silver held in suspension, and affords therefore a striking confirmation of the statement of Dupasquier, that not only gold, but silver and other opaque bodies, present this view when greatly subdivided and viewed through a clear suspending medium (*Comptes Rendus*, No. I. July 1845). It may be added, that the same hue is developed when a very dilute solution of nitrate of silver is subjected to the reducing action of a formiate.

Allusion has already been made to the production of *acetic acid* in large amount by a modification in the above process. For this purpose the powdered bichromate and the sulphuric acid, in the proportion of about 2 to 3, are to be first mixed in the retort so as to develop a large amount of free chromic acid. The alcohol is then introduced from the pipette as in the former case, and with like precautions. During the violent action that ensues, much acetic acid passes over without the aid of external heat. When the alcohol thus added amounts to about twice the weight of the bichromate employed, the action having subsided, we apply a gentle lamp heat, and obtain a large additional quantity of the acid. This we have found to be free from sulphurous acid, and to contain little more than a trace of formic acid and aldehyde.—*Silliman's Journal*, July 1846.

Formation and Preparation of Hyposulphite of Soda.

By E. F. ANTHON.

When dry sulphurous acid is passed over dry sulphuret of sodium, the substances do not act on one another; but in the presence of about 20 per cent. water the sulphurous acid is very rapidly absorbed, provided the sulphuret contain an excess of carbon, and is not fused, but only caked together. During this absorption a considerable development of heat takes place, and at the same time the sulphuret of sodium becomes quite moist. Upon this a disengagement of sulphuretted hydrogen is perceptible; and as soon as this has ceased, the product yields with water a colourless solution free from sulphuret of sodium, and which therefore soon becomes converted, on exposure to the air, into sulphite and sulphate of soda. Scarcely a quarter of an hour is requisite for obtaining small quantities, and from the crude carbonaceous mass crystallized hyposulphite of soda can readily be prepared. For technical purposes the passing the sulphurous acid into the sulphuret of sodium must be

discontinued before the evolution of sulphuretted hydrogen has quite ceased, that it may still contain a little sulphuret of sodium, and so a hyposulphite of soda be obtained which is permanent in the air.—*Buch. Rep.*, xlii. p. 20.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Precipitation of Gold in the Metallic State. By M. BARRAL.

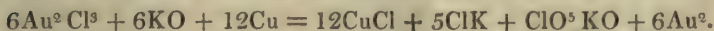
IN the memoir which I have the honour to lay before the Academy, I have examined what are the conditions on which the precipitation of gold in the metallic state on the different ordinary metals in a continuous and adherent layer depends. The solution of gold on which I have experimented is the alkaline bath of Mr. Elkington, and the simple immersion is effected in the same way as is practised in gilding by the moist process. Struck with the obscurities which still surrounded the explanation, I first sought to dispel them. The Academy will no doubt remember that Messrs. Wright and Elkington supposed that on boiling the perchloride of gold in presence of a large excess of bicarbonate of potash and organic substances, this salt was reduced to the state of protochloride. M. Dumas, in his important report on the processes of gilding of Messrs. Elkington and Ruolz, regarded this explanation as probable, and admitted that, in the gilding of brass by the moist way, the chlorine of the protochloride of gold seizes hold of 1 equiv. copper, while 1 equiv. gold is precipitated. M. Figuier has denied this explanation in his memoir on the oxygenized compounds of gold, purple of Cassius and fulminating gold*. He asserts that the protoxide of gold is precipitated as fast as it is formed, and constitutes the black deposit which is always observed at the bottom of baths in action; and he maintains that an oxide of gold is formed, containing more oxygen than auric acid, of remarkable instability and eminently suited for the deposition of gold. Thus, on the one hand, reduction of the gold and gilding by the salt at the minimum state of oxidation; on the other hand, superoxidation of the gold and gilding by the higher oxide. These are the two opposite theories, between which the balance alone can decide.

I formed a bath containing a known quantity of gold, and gilded with it a certain number of objects, then analysed the solution and the black sediment collected at the bottom, and readily found, that both in the bath, as well as in the black precipitate, there was a quantity of copper equal to Cu^2 , while Au^2 had been precipitated. This result leads me to conclude, that the agent in the gilding is either the protochloride of gold, and the reaction $\text{Au}^2\text{Cl} + 2\text{Cu} = \text{Cu}^2\text{Cl} + \text{Au}^2$, or the unknown chloride of gold intermediate between the proto- and perchloride, for we might equally well have $\text{Au}^2\text{Cl}^2 + 2\text{Cu} = 2\text{CuCl} + \text{Au}^2$.

* *Chem. Gaz.*, vol. ii. p. 277.

In the black precipitate, considered by M. Figuier as the protoxide of gold, and by other chemists as pulverulent metallic gold, I have found on analysis carbonate of lime, oxide of copper, and purple of Cassius. Carbonate of lime was derived from the water and the bicarbonate of potash employed, and the purple of Cassius from the tin forming the solder of the gilt objects.

On examining the solution after the gilding, I found, as M. Figuier had done, that the gold in it was in the state of a higher chloride or oxide, and I have shown that the gilding is independent of the mixed organic substances, and that the potash only acts an important part, that of absorbing the excess of chlorine. I have thus been led to continue the bath as it were indefinitely, which hitherto had only been employed for one operation. Perchloride of gold is added in proportion as the bath becomes exhausted until the whole of the potash is converted into chloride of potassium and chlorate of potash; the bath is then again rendered efficacious by adding to it bicarbonate of potash. The reaction exerted on the chlorine by the potash only takes place at the moment of the gilding, and is clearly explained by the following equation:—



As gilding by immersion is nothing more than a chemical reaction, founded on Bergmann's law of the precipitation of metals, and like every chemical action liberates electricity, I was led to think that it would be possible to gild by immersion almost all the metals to any thickness, profiting by this liberated electricity. Some experiments on the gilding of silver by M. Normand, and the researches of M. Frankenstein on electro-chemical gilding by the action of a single pair, without the employment of a diaphragm, in baths employed for gilding by the battery, pointed out the possibility of realizing this idea.

From the experiments made by M. d'Arcet on gilding by mercury and by the moist way, executed by professional gilders, M. Dumas was led to state that the best gilding by the moist process, having fixed 0.0422 grm. gold to the square decimetre, and the worst with quicksilver, having taken 0.0428, it is evident that gilding by the moist process scarcely attains, in the most favourable case, to the degree of thickness which the worst gilding with quicksilver necessarily attains. I at first thought that if the gilders who executed the specimens examined by M. d'Arcet had allowed them to remain for a longer time in the bath, they would have acquired a thicker layer of gold; experiment has shown that the maximum thickness which it is possible to attain in gilding by the moist process had not been realized. This result agrees with that obtained by M. Becquerel, in his researches on the influence of polishing the surface in gilding by the moist process; and I have confirmed the principle, that plates of copper, polished with the greatest care, are precisely those which take the least gold.

Thus, on the one hand, but a very thin layer of gold is deposited by immersion on a well-polished surface, evidently because the deposited gold being in a continuous and highly-adherent layer, the

copper can no longer dissolve; and, as we have shown in our memoir, Au^2 is only precipitated in proportion as Cu^2 is dissolved. On the contrary, a badly-polished surface, but well tempered and cleansed, so as not to be protected from chemical action, by a layer of grease, may be coated by immersion with a layer of gold, the thickness of which is solely limited by the quantity of gold contained in the solution; because the deposited gold being in an interrupted and frequently non-adherent layer, the exposed copper can dissolve, and Au^2 is precipitated as long as there is any Cu^2 . This being established, let us immerse at the same time some well-polished and some badly-polished copper, connected by a copper wire, in Elkington's bath. The last copper will produce a chemical action, a pulverulent deposit of gold, a permanent solution of copper, and lastly a galvanic current. On the first copper there will be at the commencement a deposition of gold by the ordinary law of metallic precipitation, and subsequently a deposit of gold, due to electro-chemical action; for the badly-polished copper becomes the positive pole, and the well-polished copper the negative pole, of the voltaic element thus constituted.

I have succeeded, according to this principle, in gilding of any thickness, with the most beautiful tints and colours, copper, silver, platina, iron, and lastly *gold* itself, in Elkington's bath, by the simple immersion of the metals in the presence of copper, zinc or lead.—*Comptes Rendus*, July 6, 1846.

PATENT.

Patent granted to Eden Thomas Jones, Bristol, for Improvements in the Apparatus used in the Concentration of Sulphuric Acid.

CONSIDERABLE inconvenience has frequently been experienced in the ordinary process of concentrating sulphuric acid in glass vessels, from the frequent breaking of the glass vessels employed in the operation, entailing thereby a loss of the acid (to the great annoyance of the neighbourhood); and from the necessity of maintaining a high degree of temperature in the laboratory, to defend the glass vessels from all drafts or currents of cold air, which prove so destructive to the vessels when they are highly heated, great care is required. To remedy these inconveniences, the patentee employs a vessel which he terms a protector, made of sheet iron, tin, or other material not liable to be injured by the heat of the process; it may be cylindrical, square, or of any other figure, provided it completely envelopes the glass vessel or retort when at work; and it should be 4 or 5 inches larger in diameter and height than the glass retort, so as to enclose the latter in an atmosphere of hot air during the operation. The advantages to be derived from the application of this invention are as follows:—The process will be shortened, a considerable saving in fuel and labour will result, and the glass vessels will last longer.—Sealed Nov. 27, 1845.

THE CHEMICAL GAZETTE.

No. XCIII.—September 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Theory of Proteine. By N. LASKOWSKI.

THE author endeavours, in the following investigation, which was made in Liebig's laboratory, to show that the proteine, prepared accurately according to Mulder's direction, is not free from sulphur; that, in fact, it cannot be obtained free from sulphur, and that accordingly the whole theory of proteine falls to the ground. The author commences his treatise by submitting Mulder's analyses to a fresh revision, in order to show how the least differences must essentially modify Mulder's formulæ; and how, according to the results of the analyses themselves, they can be constructed in a different manner. The analyses of caseine and crystalline afford an instance:—

	Caseine.			Crystalline.		
	Found.	Equiv.	Calculated.	Found.	Equiv.	Calculated.
Carbon* ..	54.96	400	55.10	55.39	600	55.16
Hydrogen..	7.15	310	6.97	6.94	465	6.98
Nitrogen ..	15.80	50	15.95	16.51	275	15.97
Oxygen....	21.73	120	21.62	20.91	172	21.65
Sulphur....	0.36	1	0.36	0.25	1	0.24

The per-centage results found in the analysis of crystalline contain more carbon than the calculated ones; and yet on calculating the formula, 17 eqivs. carbon too little are obtained. Had Mulder found only 0.24 per cent. sulphur instead of 0.25, we should have 7 eqivs. carbon more than the theory requires. In this case there would also be 1 equiv. hydrogen and 3 eqivs. nitrogen too many, and only 5 eqivs. oxygen too few.

The following are the results of Mulder's analyses, upon which he based the formulæ of the other proteine compounds:—

	Fibrine from ox-blood.	Albumen from eggs.	Equiv. Calculated.		Albumen from blood-serum.		
C ..	54.56	54.48	400	54.90	54.84	400	54.70
H ..	6.90	7.01	310	6.95	7.09	310	6.92
N ..	15.72	15.70	50	15.89	15.83	50	15.84
O ..	22.13	22.00	120	21.55	21.23	120	21.47
P ..	0.33	0.43	$\frac{1}{2}$	0.35	0.33	$\frac{1}{2}$	0.35
S ..	0.36	0.38	1	0.36	0.68	2	0.72

* C = 76.437.

If we compare the per-centage results found with those calculated, it is seen that, with the exception of the sulphur, the numbers obtained in the analyses of the fibrine and of the egg-albumen agree more closely with those calculated according to the formula for the blood-albumen than with the theoretic numbers corresponding with their own formula; and *vice versa*, the numbers found for the blood-albumen coincide much more with those calculated according to the formula of fibrine and egg-albumen than with those deduced from Mulder's formula for blood-albumen. If we calculate the equivalents from the above numbers, we obtain in the case of fibrine, 24 equivs. C, $18\frac{1}{2}$ equiv. H, 3 equivs. N, 12 equivs. O, and $\frac{1}{15}$ equiv. S too much. The per-centage numbers found for egg-albumen yield 23 equivs. C, 13 equivs. H, 3 equivs. N, and 4 equivs. O too little, and $\frac{1}{12}$ equiv. P too much. With albumen from the serum of the blood, we find $26\frac{1}{2}$ equivs. C, $27\frac{1}{2}$ equivs. H, 3 equivs. N, and 6 equivs. O too much.

With respect to vegetable gluten, Mulder found,—

	I.	II.	Equiv.	Calculated.
Carbon.....	54.75	54.93	400	54.89
Hydrogen	6.99	7.11	310	6.94
Nitrogen	15.71	15.71	50	15.90
Oxygen	21.93	21.68	120	21.55
Sulphur	0.62	0.57	2	0.72

If we calculate in this instance the equivalents from the per-centage results, and take sulphur = 2, we find in I. 65 equivs. C, 53 equivs. H, 8 equivs. N, and 22 equivs. O too much. Now since vegetable gluten contains, according to Mulder, 10 equivs. proteine, the analyses are either incorrect, or the proteine contained in vegetable gluten is composed according to the formula $C^{46} H^{36} N^{\frac{5}{2}} O^{14}$. In calculating the analysis II., we obtain 107 equivs. C, 92 equivs. H, $12\frac{1}{2}$ equivs. N, and 33 equivs. O too much. According to this, the proteine contained in vegetable gluten would be represented by the formula $C^{51} H^{40} N^6 O^{15}$.

If we calculate Mulder's analyses according to the corrected atomic weights (H = 1, C = 6, N = 14, S = 16), we obtain—

	Caseine.	Crystalline.	Fibrine.	Egg-albumen.	Blood-albumen.	Vegetable gluten.	
	I.	II.	III.	IV.	V.	VI.	VII.
C ..	54.207	54.629	53.810	53.731	54.086	53.998	54.175
H ..	7.160	6.950	6.910	7.020	7.100	7.009	7.120
N ..	15.618	16.320	15.539	15.520	15.650	15.530	15.530
O ..	22.651	21.852	23.052	22.921	22.157	22.845	22.607
P ..	0.000	0.000	0.330	0.430	0.330	0.000	0.000
S ..	0.359	0.249	0.359	0.378	0.677	0.618	0.568

In these numbers we everywhere find $\frac{3}{4}$ per cent. carbon, and nearly $\frac{1}{5}$ per cent. nitrogen, less than in those calculated according to the old atomic weights; on this account therefore the per-centage amount of oxygen is increased more than $\frac{2}{100}$ per cent., which in the formula makes 1 equiv. oxygen for every equivalent of proteine.

If we calculate the formula for proteine according to these numbers, leaving out the sulphur and phosphorus, we obtain—

	I.	II.	III.	IV.	V.	VI.	VII.	Mean.
Carbon	40	39	43	38	43	47	51	43
Hydrogen. . .	32	30	33	$29\frac{1}{2}$	34	$36\frac{1}{2}$	40	$33\frac{1}{2}$
Nitrogen . .	5	5	$5\frac{1}{2}$	$4\frac{1}{2}$	$5\frac{1}{2}$	$5\frac{1}{2}$	6	5
Oxygen. . . .	13	12	14	12	13	15	16	14

Moreover it must be borne in mind, that no formulæ, properly speaking, can be advanced for the albuminous bodies, until it has been ascertained with accuracy what quantities of inorganic constituents, especially phosphate of lime, they always contain. Simon obtained from albumen which had been separated from its lead compound 1·2 per cent. phosphate of lime; J. Vogel obtained from the albumen of a hen's egg 2·33 per cent. ash, consisting of phosphate of lime with some sulphate of lime. Mulder found in egg-albumen 2·13 per cent. ash. According to Berzelius, caseine coagulated with rennet yields 6·5 per cent. ash; Simon obtained from the caseine of cow's milk 7·0 per cent. ash, from that of woman's milk 5·0 per cent.; Mulder found in caseine 3·8 per cent. ash. Berzelius found in fibrine 0·66 per cent. ash; Simon, 1·5–2·0; Vogel, 2·66; Mulder, 8·5; but in that which had been digested with spirit, only 0·9 per cent.

Mulder calculated the atomic weight of proteine from the lead and silver compounds, and also from the proteo-sulphuric acid, proteo-chlorous and proteo-tannic acids. He obtained from the latter determinations, the following numbers:—I. 5508; II. 5605; III. 5906; IV. 5682; V. 5310; VI. 5768; VII. 5724; VIII. 5517. It is seen that the found atomic weights agree as little with one another as with the calculated atomic weight 5530. But it is moreover remarkable, that the found atomic weights, with the exception of VI. and II., agree more closely with the atomic weight of egg-albumen and fibrine, from which the compound examined had been obtained, than with that calculated for proteine.

All the above differences, which result in the formulæ on calculating two of Mulder's analyses of the same substance, are owing to a bad determination of the sulphur, which gave rise to an error greater in proportion to the small amount of sulphur present, which in the formula was always taken = 1; and for this reason a revision of the amount of sulphur contained in the proteine compounds was of the greatest importance.

It has been admitted that, in treating fibrine and albumen with solution of potash, the phosphorus is obtained as phosphate of potash, the sulphur as sulphuret of potassium. If this is to happen by a mere exchange of elements, for each equivalent of phosphorus 5 equivs. sulphur must separate from the albuminous body, in order, by forming sulphuret of potassium, to yield the 5 equivs. O requisite for the production of PO^5 ; but since the sulphur and phosphorus are not contained in these proportions in the proteine compounds, water must be decomposed in order to form the phosphoric acid,

and hydrogen gas should be liberated. The same applies to the proteine compounds which contain no phosphorus; in this case the oxygen liberated by the formation of sulphuret of potassium should either be disengaged or replace the sulphur in the proteine; such an opinion would only be probable if it were proved that the whole of the oxygen of the potash converted into sulphuret of potassium has been applied to the formation of an acid of sulphur. It is moreover to be observed, that, on dissolving fibrine and albumen in caustic potash, some ammonia, which can only proceed from those bodies, is always disengaged, so that it cannot be admitted that they remain entirely undecomposed.

We have already had occasion to mention that Liebig found some sulphur in a body, which according to Mulder was binoxide of proteine*; and this led the author to examine proteine anew as to the presence of sulphur. The proteine for these experiments was prepared from egg-albumen, caseine and fibrine. The albumen was obtained by beating the albumen of a hen's egg with distilled water, then adding some muriatic acid (2 to 3 drops to each egg), filtering after subsidence of the cell-membrane through paper, precipitating the solution with absolute alcohol, and boiling the precipitate with alcohol and æther to remove the fat. For the preparation of the caseine, freshly coagulated cheese was well-washed with distilled water, dissolved in a very weak solution of carbonate of soda, and the solution set aside for the cream to separate. After removing the cream, the strained solution was precipitated with acetic acid; the precipitate kneaded so long with hot distilled water as the latter passed through turbid, and then extracted with boiling alcohol and æther. The fibrine obtained by beating ox-blood was freed by washing with water from colouring matter, and then from fat by alcohol and æther. The following methods were adopted to detect the sulphur:—

1. The albuminous substance is dissolved in solution of potash of 1·45 spec. grav.; or, when it is already in solution, mixed with so much caustic potash, that on the addition of a few drops of a solution of basic or neutral acetate of lead no permanent white precipitate is formed. After the addition of the lead solution the liquid is boiled, when the colour produced by the sulphuret of lead indicates the sulphur. But since the alkaline solutions of albuminous bodies become brown on boiling, even without any addition of lead, the following plan should be adopted in all doubtful cases. The alkaline solution is divided into two equal portions, which are poured into two test-tubes of the same size; upon this solution of lead is added only to one of the tubes, and then both tubes heated over the same flame for the same time. After sufficient boiling the colour of the liquids in the two tubes is compared, when, if the substance contain sulphur, a sediment of sulphuret of lead is frequently found in that portion to which a solution of lead had been added.

2. Still more delicate, and always to be employed in those cases where the above test leaves any doubt, is the following:—Some of

* See page 101 of the present volume.

the substance is heated in a test-tube with a piece of hydrate of potash to decomposition; some muriatic acid (which should, of course, be perfectly free from nitric acid) poured over it, and the tube covered with a piece of bibulous paper which has been moistened with a solution of lead; if the substance contained sulphur, the lead paper is coloured by the liberated sulphuretted hydrogen.

According to Mulder, proteine is obtained in the form of flakes, when boiled albumen is dissolved in dilute alkali, and the latter neutralized with an acid. In like manner it is prepared from corn-flour, by freeing it from starch by kneading under water, dissolving it in dilute solution of potash, and precipitating with an acid. Liebig however found, that when albumen is dissolved in a weak solution of caustic potash, and solution of lead then added to it, there is no reaction of sulphuret of potassium perceptible; and that the precipitate formed by acetic acid in such a solution contains all the sulphur of the substance which had been dissolved in the solution of potash. The author made some similar experiments, but in the following way:—He digested coagulated albumen with solution of potash of 1.45 spec. grav., for 24 hours, at a temperature of 57° to 59° . On adding, after this interval, a solution of acetate of lead to the liquid, it merely became faintly brown; but when boiled it became perfectly black, from sulphuret of lead. It is however usually stated, that in preparing proteine, a solution of albumen, or of any other proteine compound, should be heated in weak or moderately strong solution of potash to 122° , or that it should be dissolved at this temperature and then precipitated with acetic acid. Now when albumen from an egg, or the boiled white of a hen's egg, is dissolved in strong or weak solution of potash, and heated from a quarter of an hour to 3 hours to 122° , an excess of acetic acid added to a portion of the solution, poured into a test-tube, and the tube covered with paper moistened with solution of lead, the latter is found to become coloured after a few minutes. If, to another portion of the solution a few drops of solution of lead are added, the presence of sulphur is rendered perceptible. There is no doubt therefore that, on digesting albumen with a solution of potash at 122° , sulphuret of potassium is formed; but that the whole of the sulphur is not obtained as sulphuret of potassium is evident from the fact, that on boiling the sample to which solution of lead has been added, or on boiling a new portion of the solution for a few minutes, and then adding solution of lead, a liquid is obtained, in both cases, which becomes perfectly black from sulphuret of lead. If the solution of albumen in potash which has been exposed to a temperature of 122° is thrown down with acetic acid, the precipitate washed, dissolved in strong potash ley, solution of lead added and boiled, the presence of sulphur is just as marked as if albumen had been used for the experiment. The same likewise applies to caseine and fibrine, only with these substances the reaction is not so strong; so that it may even be concluded, from a qualitative examination, that the albumen of hen's eggs contains more sulphur than fibrine and caseine. If, for instance, equal quantities of caseine and of Mulder's proteine,

obtained from egg-albumen, are each submitted in a separate tube to the moist sulphur-test, and the colour of the two liquids then compared, it will be found that, while the solution of proteine is strongly blackened by sulphuret of lead, that of the caseine is merely brown. To ascertain at what temperature the desulphuration supposed by Mulder to be effected by solution of potash takes place, the author heated solutions of albumen of egg in caustic potash from 122° to 216° ; and after each rise of 9° submitted it to the sulphur-test, the solution having been kept at the temperature from 15 to 25 minutes. It was now found that the intensity of the sulphur-reaction is proportional to the temperature; on the contrary, the quantity of the precipitate produced by acetic acid, and exhibiting the external properties of proteine or albumen, is in inverse proportion to the temperature; and that, consequently, as soon as the whole of the sulphur is converted into sulphuret of potassium, no proteine-like precipitate is obtained. The author moreover found that the desulphuration does not happen before boiling-point is attained. The solutions, digested at 176° – 194° , yielded, on saturation with acetic acid, precipitates which still exhibited the presence of sulphur. Even at the boiling-point some time is required before the apparent desulphuration takes place, the length of which may depend on the concentration of the solution of potash.

Since no proteine could be obtained by treatment with solution of potash, some albumen, dissolved in caustic potash, was heated with chloride of ammonium, when sulphuret of ammonium was disengaged; but the whole of the sulphur could not be removed by boiling for several hours. On the supposition that very dilute alkaline solutions might effect the removal of the sulphur from the albumen, and that by employing them at a higher temperature it might be more easy to avoid any possible decomposition of the proteine, recently-precipitated finely-divided albumen was mixed with a large quantity of water, and so much solution of potash added, with constant stirring, as sufficed to dissolve it. Upon this a few drops more of solution of potash were added, and the solution then heated until the reaction of sulphur no longer increased. Hydrated oxide of bismuth, or finely-divided metallic silver, was now added, and the liquid again heated, with frequent agitation, until a filtered sample presented no reaction of sulphur on being boiled with a strong solution of potash and oxide of lead. If to the desulphuretted alkaline solution so much acetic acid is added that the liquid has a faint acid reaction, a white precipitate is obtained. If this is collected on a filter and washed with water, a substance is obtained which dries in the air to a transparent, dark yellow, friable mass. This body does not dissolve even in boiling water, and floats as if melted on the surface, losing its transparency, which however again appears on desiccation. It is not soluble in absolute alcohol. On combustion it yielded 54.6 per cent. C, 6.0 H, 23.9 N, and 15.5 per cent. O. If the liquid filtered from the substance precipitated by acetic acid is evaporated to a syrupy consistence and then mixed with an excess of alcohol, a second white precipitate is obtained, which resembles

in its external appearance that thrown down by acetic acid, only that it is very soluble in water.

When finely-divided caseine is dissolved by a gentle heat in weak caustic potash, and the solution heated until the precipitate produced by acetic acid in a hot sample has a melted resinous appearance and redissolves on the addition of alcohol, and the hot solution is slightly supersaturated with acetic acid, a white or yellowish tenacious body separates, which hardens in the air to a yellowish-brown transparent mass, and very much resembles biliary resin. This body is soluble in water, and is again precipitated from it by acids. When boiled with alcohol it deliquesces, and a whey-like solution is obtained, from which however the body immediately separates on cooling. It dissolves readily and entirely in barytic water, and may in this way be separated into two distinct compounds. For this purpose it is dissolved by boiling in barytic water, and a current of carbonic acid, which has been washed by passing through bicarbonate of soda, conveyed through the hot solution as long as any precipitation of carbonate of barytes occurs. The liquid is then decanted from the precipitate, heated to boiling, and the carbonate of barytes separated in this operation removed by filtration, and the solution evaporated on the water-bath. During evaporation crystalline pellicles separate; as soon as no more are formed, the crystals are collected and the mother-ley further evaporated. This dries at last to a transparent, brittle, yellowish mass, greatly resembling barley-sugar, which dissolves without any residue in water to a clear solution, from which acetic and muriatic acids throw down a caseous organic substance. The crystals obtained during the evaporation have a warty appearance under the microscope; when heated alone, they become very black; they are very sparingly, or not at all, soluble in water and barytic water. When water is poured over them, and muriatic and acetic acid then added, a caseous organic substance likewise separates in this instance. The above bodies, when fused with hydrate of potash, and the addition of some muriatic acid, all yielded, excepting the one contained in the crystalline barytes compound, some sulphuretted hydrogen; but the quantity was so excessively minute, that the sulphur detected in this manner may have arisen from some foreign admixture (perhaps from a trace of non-desulphurated albumen or caseine).—Liebig's *Annalen*, lviii. p. 129.

On the Formation of the Sulphite of Nitric Oxide. By M. ANTHON.

On disengaging, at a low temperature, nitric oxide from dilute nitric acid and copper, and passing this slowly over concentrated sulphuric acid in a tube containing air, the author observed, at the margin of the stratum of sulphuric acid, a white crystalline mass, the formation of which however apparently ceased as soon as the whole of the atmospheric air had been expelled by the vapours of the nitric oxide. But when oxide of nitrogen and atmospheric air were again passed into the tube, yellow vapours immediately became perceptible, and the crystalline mass increased considerably. The

colourless gas, on its exit from the apparatus, had no longer any odour; while before, when no access of air was possible, the disengaged gas immediately diffused suffocating vapours of nitrous acid. At last the sulphuric acid was entirely converted into a crystalline mass. Taken out of the apparatus and moistened with water, a violent disengagement of colourless nitric oxide took place, and it became coloured green.

100 grms. yielded, on decomposition with water, 290–300 cub. cent. of colourless nitric oxide; while 100 grms. concentrated sulphuric acid, into which a constant current of pure nitric oxide had been passed for 32 hours, and to which only a little atmospheric air had access at the commencement, afforded under the same circumstances only 29.5 cub. cent. of colourless nitric oxide. When dry nitrous acid, obtained by heating dry nitrate of lead, was passed into warm sulphuric acid of 1.84 spec. grav., the gas was rapidly absorbed, and the acid became thick, and solidified on cooling almost entirely to a crystalline mass, which behaved in precisely the same manner as that above described.—*Buch. Rep.*, xlii. p. 13.

Examination of Chelidonic Acid and its Salts. By J. U. LERCH.

[Concluded from p. 313.]

Yellow Tribasic Chelidonates.—These are formed from the bibasic salts by treatment with ammonia, or any other caustic alkali. If a quantity of carbonate of potash be added to bibasic chelidonate of lime, just sufficient to precipitate the whole of the lime, and if the solutions are not dilute, the whole of the lime is not eliminated, and a bibasic potash salt is not obtained, but 1 atom of lime remains with the 2 atoms of potash added in combination with the acid, and a tribasic salt is formed with two different bases. When the solution is now strongly diluted, the atom of CaO does not separate; but if dilute solutions be used at the commencement and no heat employed, the whole of the lime is thrown down, and a bibasic salt of potash formed. By adding carbonate of potash in excess to the tribasic potash-lime salt, and also by treatment with carbonate of ammonia, in the first case a tribasic, and in the latter a bibasic potash salt is obtained. The tribasic salts may likewise be prepared by double decomposition of a bibasic salt of an alkali to which ammonia has been added, for instance by means of the lime salt with other salts, whose oxides yield with chelidonic acid an insoluble tribasic salt. In this case the solutions must be likewise dilute, in order to prevent the formation of a double salt. The tribasic salts of the alkalies are readily soluble in water, and crystallize; those of the other bases are sparingly soluble or insoluble, and form precipitates. Like the bibasic salts, they contain several atoms of water of crystallization, which they part with only at a higher temperature than 212°. The silver salt is likewise anhydrous. They are decomposed by acids, and also by long solution in water. The salts of the alkalies gradually absorb carbonic acid, and are decomposed into a carbonate and bibasic salt.

Tribasic Chelidonate of Baryta.—The bibasic lime salt was dissolved in water, a sufficient quantity of ammonia added to it, and slightly warmed; the colourless solution of the lime salt turns yellow on the addition of ammonia and the application of heat. This yellow liquid was now precipitated with chloride of barium, and the lemon-coloured precipitate quickly filtered and washed. It forms a lemon-coloured powder, which dissolves but sparingly in water, and not at all in spirit; it is not altered by exposure to the air, absorbs no carbonic acid, and is consequently one of the best tribasic salts that can be readily prepared pure. It also contains water of crystallization, which is not expelled at 212° . It yielded on analysis—

Carbon.....	18.88	14 =	1050.0	19.06
Hydrogen	1.72	7	87.5	1.59
Oxygen	27.60	15	1500.0	27.24
Baryta	51.80	3	2870.6	52.11

The formula of the salt is therefore $C^{14}H^2O^{10} + 3BaO + 5aq$.

Tribasic Chelidonate of Lime.—When the crystallized bibasic lime salt is boiled with ammonia, it becomes yellow with scarcely any alteration of form, and is converted into a tribasic salt. When lime water is added in the cold to a solution of the bibasic lime salt, no alteration is perceptible; the previously neutral liquid has an alkaline reaction from the addition of lime water; but if the liquid be heated to boiling, it turns yellow, and the formation of a yellow precipitate occurs; at the same time the alkaline reaction disappears. The yellow salt however is always more or less mixed with carbonate of lime, the formation of which it is difficult to prevent in this treatment. The salt forms a yellow amorphous powder, feeling like starch. Under the microscope it exhibits the same form as particles of starch; it dissolves with difficulty in water and not in spirit; it is decomposed by acids, like the other salts. On analysis it yielded—

Carbon.....	28.84	14 =	1050.0	28.48
Hydrogen	2.75	7	87.5	2.37
Oxygen	39.53	15	1500.0	40.67
Lime	28.88	3	1050.0	28.48

It resembles therefore the barytic salt in its composition, being $C^{14}H^2O^{10} + 3CaO + 5aq$.

Tribasic Chelidonate of Lead.—By treating the white bibasic lead salt with ammonia, it is converted into a yellow tribasic salt. When a solution of the bibasic lime salt is treated in the cold with basic acetate of lead, a yellowish-white flocculent precipitate forms, which is the tribasic lead salt with 2 atoms of water of crystallization. When the solutions are mixed boiling, a deep yellow precipitate is immediately produced, which is the anhydrous tribasic salt. It forms when dry a lemon-coloured amorphous powder, the colour of which becomes dark, slightly orange, when any of the basic lead salt is mixed with it. It is insoluble in water and in spirit, soluble in salts of lead. It yielded on analysis 15.90 C, 0.52 H, and 67.06 per cent. oxide of lead. The formula of the anhydrous salt is there-

fore $C^{14}H^2O^{10} + 3PbO$; that of the hydrated, $C^{14}H^2O^{10} + 3PbO + 2aq$.

Tribasic Chelidonate of Silver.—This salt was prepared by precipitating with nitrate of silver the bibasic lime salt to which ammonia had been added, and also the pure yellow tribasic lime salt. In both cases a beautiful lemon-coloured precipitate of a tribasic silver salt resulted, which however soon decomposed. It acquires a dirty greenish colour during filtration, and the entire mass becomes yellowish-brown while drying *in vacuo* over sulphuric acid, and then no longer dissolves entirely in ammonia. The silver salt is anhydrous, and is represented by the formula $C^{14}H^2O^{10} + 3AgO$.

A chelidonate with two bases, oxide of silver and lime, was obtained by mixing a concentrated solution of nitrate of silver with a concentrated solution of the bibasic lime salt to which ammonia had been added. This salt is of a lighter colour than the preceding, and far more stable; it is scarcely altered on drying, and is decomposed only after long boiling with water. It yielded on analysis—

Carbon	19.47	14 =	1050	19.71
Hydrogen	0.76	2	25	0.47
Oxygen		10	1000	18.78
Oxide of silver ..	54.04	2	2900	54.46
Lime		1	350	6.58

Its formula is $C^{14}H^2O^{10} + CaO, 2AgO$.

Chelidonate of Iron.—Chelidonic acid dissolves iron with evolution of hydrogen, forming chelidonate of the protoxide of iron, which remains dissolved in the liquid; but on evaporating the solution it becomes higher oxidized, and subsides in the form of dirty yellow flakes. On precipitating the bibasic salt of soda with perchloride of iron, a dirty yellow precipitate with a reddish tint formed, which was almost insoluble in water, but soluble in acids and in an excess of perchloride of iron. The salt is not altered by exposure to the air at 212° ; at a higher temperature it may be set light to, and then burns with a shower of sparks. Its formula is $C^{14}H^2O^{10} + Fe^2O^3$. If an excess of perchloride of iron be added to a solution of a chelidonate of potash or soda, chelidonate of iron is precipitated, but the greater portion remains in the solution. The filtered liquid is clear and of a light yellow colour; it gradually becomes darker, and after some time perfectly dark brownish-black and opaque. If the liquid be kept for a still longer time, it again gradually loses the dark colour, and the liquid becomes yellow, and at last nearly colourless; it passes through these remarkable changes more rapidly when heated. By the addition of some ammonia to the dark brown opaque fluid, a rusty brown compound is precipitated, which becomes black by a larger addition of ammonia, probably from the reduction of the peroxide of iron; when the liquid has again become transparent and colourless, ammonia produces a reddish-brown deposit, which contains 7.32 per cent. C, 1.56 H, 33.56 O, and 57.56 Fe^2O^3 .

Chelidonic acid likewise enters into combination with oxide of

chromium and oxide of antimony; the first is a beautiful green precipitate, which forms only after the addition of ammonia, or on heating the solutions of chrome-alum and chelidonate.

Tribasic Chelidonate of Potash.—A concentrated solution of the bibasic potash salt becomes yellow on the addition of an alcoholic solution of potash, depositing yellow crystals, which, after frequent washing with warm alcohol to remove the free potash, cake together to a soft amber-coloured mass. On dissolving this in the least quantity of boiling water, the salt crystallizes on cooling from it. It is dark yellow, at first effloresces in the air, absorbs carbonic acid, then becomes moist, and the yellow colour disappears. The pure salt has a neutral reaction. When boiled with an excess of caustic potash, oxalate of potash may be detected in it. The soda salt behaves analogous to the yellow potash salt, but no yellow tribasic ammonia salt could be prepared.

Monobasic Chelidonates.—When a third part chelidonic acid is added to a solution of bibasic salt, boiled, and allowed to cool, the monobasic salt crystallizes from it, and the excess of acid remains in the solution. The same is the case with a dilute mineral acid when added to a concentrated solution of a bibasic chelidonate; the monobasic salt separates in a crystalline state. When a considerable excess of acid is used, or the bibasic salt is dissolved by boiling, an acid salt, containing 1 atom of monobasic salt to 1 atom of hydrated chelidonic acid, crystallizes from the acid solution. No monobasic salts with oxide of silver and lead appear to exist, as a bibasic salt is immediately precipitated, even from chelidonic acid itself, by nitrate of silver or lead; and both these oxides may be again separated from the chelidonic acid by concentrated nitric acid without a monobasic or acid chelidonate being formed. The monobasic salts are not permanent; they are decomposed by frequent crystallization into acid and bibasic salts, which latter separate in crystals, while the former remain in solution. They are colourless, crystallize in delicate needles like the bibasic, but have an acid reaction, and likewise contain water of crystallization, which they do not part with at 212° . The soda salt was prepared by dissolving the bibasic soda salt in chelidonic acid; it crystallized in slender needles, and was purified by crystallization. On analysis it gave—

Carbon.....	34.37	14	=	1050.0	34.67
Hydrogen.....	3.16	7		87.5	2.88
Oxygen.....	49.81	15		1500.0	49.54
Soda.....	12.66	1		390.9	12.91

The formula of the salt is $C^{14}H^2O^{10} + 2HO, NaO + 3aq$.

Acid Chelidonates.—These are obtained by dissolving the bibasic salts in hot muriatic acid, from which they crystallize on cooling in slender needles or small scales, which are soluble in water and have an acid reaction. They also contain water of crystallization, which they do not part with at 212° . They are not altered by recrystallization, and the 1 atom of base can only be separated by frequent treatment with muriatic acid. The acid lime salt, dried at 212° , yielded on analysis—

Carbon.....	39.92	28 =	2100.0	39.72
Hydrogen	2.65	11	137.5	2.60
Oxygen	50.91	27	2700.0	51.07
Lime	6.52	1	350.0	6.61

The salt therefore is a combination of $C^{14}H^2O^{10}$, $2HO$, $CaO + C^{14}H^2O^{10}$, $3HO + Aq$. Analogous to this in composition is the acid salt of baryta, $C^{14}H^2O^{10}$, $2HO$, $BaO + C^{14}H^2O^{10}$, $3HO + 2aq$. The formula for the acid salt of soda is $C^{14}H^2O^{10}$, $2HO$, $NaO + C^{14}H^2O^{10}$, $3HO + 3aq$.

There is yet a lead salt to be mentioned, which contains 6 equivs. oxide of lead to 1 of acid. It is obtained by decomposing the lime salt to which ammonia has been added with boiling basic acetate of lead, and differs externally from the tribasic lead salt by its darker faintly orange colour.

Hydrate of Chelidonic Acid.—If the 3 atoms MO in the tribasic salts, which cannot be basic salts, as the silver salt as well as those of the alkalies do not admit of this view, be replaced by 3 equivs. water, we obtain for the hydrate of chelidonic acid the formula $C^{14}H^2O^{10} + 3HO$. This supposition is not confirmed by the examination of the hydrated acid, admitting that the hydrate water should not separate from the acid at 212° . The analysis of the hydrate, dried at 212° , yielded—

Carbon.....	45.37	45.13	45.70	45.40	14 =	1050	45.65
Hydrogen....	2.26	2.28	2.54	2.36	4	50	2.17
Oxygen	52.37	52.59	51.76	52.24	12	1200	52.18

The acid dried at 212° differs from the anhydrous acid contained in the salts by the elements of 2 equivs. water. From the examination of its combinations with bases, it is evident that it combines with 3 equivs. base to form a neutral salt; it must therefore also contain 3 equivs. basic water capable of being replaced by metallic oxides, but in the hydrate dried at 212° we find only 2; the third equivalent therefore of basic water, represented in the salts by 1 atom MO , is so loosely combined with the radical of the acid, that it separates even at a temperature of 212° , and escapes along with the water of crystallization. The acid crystallized by spontaneous evaporation loses, on drying at 212° , 2 equivs. water; the formula of the crystallized acid must therefore in the one case be expressed by $C^{14}H^2O^{10} + 3HO + Aq$, in the other case by $C^{14}H^2O^{10} + 3HO + 2aq$. In this property of the hydrated acid, of parting at 212° with 1 atom of basic water, chelidonic acid forms an exception from all other organic acids.

There are however other acids which lose their hydrate water at higher temperatures in part, or even altogether; such is the case with succinic acid at 284° ; it gives off the half, $\frac{1}{2}$ an atom of its hydrate water; it may also be obtained anhydrous without losing the properties of an acid; it reabsorbs the lost hydrate water on solution in water. The same applies to itaconic acid. The property of parting with a portion of hydrate water is exhibited in a high degree by phosphoric acid. It can give off 1 or 2 atoms of its hy-

drate water at certain temperatures, and its mono- and bibasic salts, from which the basic water can also be separated, exhibit the same property. It was to be supposed that the third atom of basic water in the bibasic chelidonates would be expelled at a certain temperature, as with the hydrated acid. The author found that in the soda and lime salts the whole of the water of crystallization goes off between 302° – 320° , and that the dried salt still contains 1 atom basic water. The atom of basic water, which the acid so readily parts with at 212° , cannot be expelled from the salts by a temperature of 302° – 320° ; this atom of water in the bibasic salts cannot therefore be the one which the hydrated acid loses at 212° ; and we must consequently form the following opinion respecting this third atom of water:—According to general chemical laws, the 3 atoms of water in the hydrated chelidonic acid cannot all be combined with the same force; the third atom is evidently most loosely combined, the second more so than the first; now when hydrated chelidonic acid is partially saturated with a fixed base, that atom of water which is most loosely combined is first replaced. A metallic oxide therefore, which naturally cannot be expelled at 212° , has taken the place of the third atom of water; the other 2 atoms of water however cannot be separated at 212° , as is proved by the hydrated acid. The monobasic soda salt is also an example. If the third atom of basic water is replaced by a volatile base, as ammonia, the ammonia is expelled at 212° , as is the water. When a second atom of the metallic oxide is added to the hydrated chelidonic acid, the looser of the 2 still remaining atoms of water, the second atom is displaced. That atom of water which is contained in the salts with 2 atoms of fixed base must therefore be the first of the hydrate water, which is most strongly combined, and cannot be expelled at 212° , just as with the hydrated acid. This view appears to stand in contradiction to the results afforded by the ammonia salt. According to it, the ammonia salt should have the composition $\overline{\text{Che}} + \text{HO} \cdot 2\text{AmO}$; the water contained in it would be, as in the lime salt, the first atom in the hydrated acid, and should therefore not be expelled at 212° ; on the contrary, the 1 atom of AmO replacing the third atom of basic water, should have been liberated at 212° , and the ammonia salt have yielded the formula $\overline{\text{Che}} + \text{HO} \cdot \text{AmO}$. This indeed actually occurs; but towards the end of the process the ammonia salt $\overline{\text{Che}} + \text{HO} \cdot \text{AmO}$ exists in the liquid with free ammonia, which now evidently replaces the first atom of water, and converts the ammonia salt into $\overline{\text{Che}} + \text{AmO} + \text{AmO}$, and then combines with the remaining atoms of water on crystallization. This last explanation supposes the oxide of ammonium to be capable of also expelling the first atom of basic water and of occupying its place. If we attempt to prepare the yellow tribasic salt $\overline{\text{Che}} + 3\text{AmO}$, it does not succeed, from the slight affinity of the anhydrous chelidonic acid to a third atom of a volatile base. Meconic acid does not part with a third atom of hydrate water at 212° , and therefore a yellow tribasic meconate of ammonia can be obtained; but if ammonia be added to

a bibasic chelidonate, for instance of lime, the liquid instantly becomes coloured yellow, that is, the first atom of water is replaced by oxide of ammonium; and if the liquid be treated now with a salt of barytes, lead or silver, a precipitate of the tribasic salt of the corresponding base is formed. Nevertheless the 1 atom of basic water contained in them can be expelled from the bibasic salts; the salts with fixed base require a temperature of 392° for this to occur. The acid in the salts undergoes no decomposition by drying at this high temperature; they are not perceptibly altered in external appearance, but only coloured somewhat yellowish. The bibasic lead salt gave in this experiment—

Carbon	20.88	14 =	1050	21.58
Hydrogen	0.68	2	25	0.51
Oxygen	..	10	1000	20.57
Oxide of lead	..	2	2789	57.34

The lead salt has parted with the first atom of basic water along with its 1 atom of water of crystallization, and is $C^{14}H^2O^{10} + 2PbO$. The lime salt behaves in the same way at 392° ; it loses along with its 5 atoms of water of crystallization, which it parts with already at 302° , also its first atom of basic water, and is $C^{11}H^2O^{10} + 2CaO$. The ammonia salt, dried at 212° , has the same formula as the lead and lime salt at 212° , and might be expressed, as well as the acid dried at 212° , by the simple formula $C^7H^2O^5 + MO$.

Chelidonic acid calls so forcibly to mind meconic acid, that it was to be suspected *à priori* that the two would not differ much in their composition. Both are tribasic acids; the tribasic salts of both are equally coloured yellow; the bibasic, white and crystalline; they are both decomposed at a high temperature, with evolution of pure carbonic acid gas, into other acids. On comparing the composition of the anhydrous acids with one another, we find that chelidonic acid differs from meconic by containing 1 equiv. more hydrogen and 1 equiv. less oxygen.—*Ann. der Chem. und Pharm.*, lvii. p. 273.

On the Respiration of Frogs. By R. F. MARCHAND.

[Continued from vol. iii. page 167.]

The author's former investigations led to the following results:—1st, that in a normal condition frogs absorb a larger quantity of oxygen than is requisite to form the carbonic acid which they expire; this quantity is such, that if we suppose the excess of oxygen to be applied to the formation of water, the mean proportion of the oxygen in the carbonic acid to that in the water is as 100:25; 2nd, that the respiration is less during the night than the day, the proportions varying from 100:76.3 to 100:47.2; 3rd, that less carbonic acid than natural is formed both at a higher and at a lower temperature; 4th, that during respiration in oxygen more oxygen is absorbed than under ordinary circumstances, but nearly the same quantity of carbonic acid is formed; 5th, that the animals in hy-

drogen expire a small quantity of carbonic acid, which however may arise from the hydrogen containing a small quantity of oxygen; 6th, that the carbonic acid contained in the blood (that is, about 16-18 milligrm.) is separated by continued retention of the animal *in vacuo*; 7th, that the quantity of carbonic acid in respiration *in vacuo* is increased; and 8th, that in fasting animals progressively less oxygen is absorbed and carbonic acid separated. In his recent experiments, the author made use of the process which we have previously described, with the modification of weighing the potash-apparatus and chloride of calcium tubes together, so that in this manner many weighings were dispensed with. Instead of a Liebig's potash-apparatus, a wide tube filled with fragments of pumice-stone imbued with solution of potash was used, so that the air which passed through came into contact with the solution of potash many times. Instead of the three chloride of calcium tubes, three tubes filled with pumice-stone and sulphuric acid were used. The sulphuric acid was previously boiled in a retort until half had passed over. The residue was used.

Respiration of the Animals while Fasting.—Chossat has found that the temperature of a starving dog does not materially diminish, whence we might conclude that the animal processes continued unimpaired; the experiments of Boussingault and of the author however are opposed to this statement. This may be explained by considering that when the mass of the body is diminished less material for caloric will be consumed, but then the expired carbonic acid must diminish in the same proportion as the mass of the body; but neither is this the case, for the animal falls into a kind of lethargy, which produces a diminution of the whole respiratory action. In frogs which were kept entirely from food, Chossat found 15 months to be the longest period of the duration of life, 6 months the shortest, 9 months the average. The body, on the death of the animal, had lost as a maximum 0.59, and 0.33 as a minimum, the mean being 0.41. In warm-blooded animals the loss amounted to 0.397 on an average; thus the daily loss was tolerably uniform. Marchand's results are somewhat different: the frogs always had enough water to swim in; and moreover the observations were not continued until they died. They were weighed in 3 sections, 4 animals in each, with the cautions given by Chossat:—

I.		grms.	II.		grms.
Weight at the commencement...	466		Weight at the commencement...	314	
30 days afterwards	405		30 days afterwards	286	
68 days afterwards	346		45 days afterwards	273	
38 days afterwards	320		90 days afterwards	233	
			45 days afterwards	212	
III.		grms.			
Weight at the commencement		467			
30 days afterwards		389			
100 days afterwards		230			

If we compare the 136 days of the first series with the total loss of 146 grms., we get 1.07 grm. for each day; the loss is however by no means equally divided; for in the first 30 days it amounted to

61 grms., whereas it ought only to have amounted to 32 grms.; and in the last 38 days only 26 grms., whereas it ought to have amounted to 40·5 grms. In the second series the daily loss would be 0·57 grm.; in the third, almost exactly a gramme; but here the proportions are the same as in the first. The author gives the following table as an example of the diminution of the respiratory products in the fasting animals; it forms a sequel to that given in vol. iii. p. 165:—

Time of the experiment.	Duration of the experiment in hours.	Oxygen contained in the water.	Oxygen contained in the carbonic acid.	Oxygen absorbed.	Carbon contained in the carbonic acid.	Carbonic acid and watery vapour exhaled.	Weight of the animals after the experiment.	Weight of the animals before the experiment.
1st series (5th series of the former experiments).—4 frogs, caught July 11.								
Oct. 21	33	0·035	0·376	0·411	0·141	0·517 C 0·476 W	345·505	346·087
Nov. 29	24	0·008	0·228	0·236	0·084	0·312 C 0·945 W	319·942	320·963
2nd series (3rd series of the earlier experiments).—4 frogs, caught June 9.								
Nov. 15	24	0·023	0·194	0·217	0·072	0·266 C 0·476 W	233·010	233·535
Nov. 26	24	0·007	0·145	0·152	0·055	0·200 C 0·685 W	212·562	213·295
3rd series (4th series of the earlier experiments).—6 frogs, caught June 9.								
Nov. 17	24	0·040	0·336	0·376	0·126	0·462 C 0·377 W	329·980	330·443
3 frogs, caught in May, after fasting for 6 months.								
Nov. 17	24	0·015	0·067	0·082	...	0·092 C 0·544 W	176·284	176·826

In the latter experiment the extremely unimportant reaction which the animals exhibited is remarkable. One animal of about 60 grms. weight absorbed 1 milligramme of oxygen for each hour, whilst in former experiments 13 milligrammes were absorbed every hour by several frogs. The blood of this starved frog did not appear to differ essentially from the normal: according to J. Müller, the lymph of a starved frog does not coagulate; this does not apply to the blood. It is evident from the above four series of experiments, that the formerly-observed diminution of the quantity of oxygen which serves to oxidize the hydrogen, as regards that applied to the formation of carbonic acid, also occurs here. In the second series the proportion formerly observed is somewhat increased; so that it appears that when a certain point is attained, where for instance the proportion of the oxygen in the carbonic acid to that in the water is about as 100:6, variations above and below occur.

Respiration during the Day and the Night.—The earlier experiments were so arranged, that the animals remained in the apparatus from the morning to the evening, and from the latter again to the morning, thus for 24 hours; and each time the carbonic acid expired during the day was compared with that formed during the

night. In a more recent experiment, performed in the same manner, the 5 animals weighed 604.195 grms., and evolved in 12 hours of the day 0.5885 grm., in 12 hours of the night 0.4980 CO²; the proportion is here therefore 100 : 83.7. The animals were also much stronger than those used formerly, and were previously kept in confinement for 5 days. 6 animals = 438.690 grms., which had been caught 4 weeks before, were then treated in the same manner, except that they were first placed in the apparatus in the evening. In 12 hours of the night they yielded 0.560 grm. of carbonic acid; in the following 12 hours of the day, only 0.4015 grm.; hence as 100 : 71.7 in the night to the day. Hence the earlier results may be at least partly explained by the animals being stronger immediately after being placed in the apparatus than when they have been in it for 12 hours; so that the difference between day and night is probably not great.

*Respiration in Vacuo**.—The author has made 2 more experiments upon this point. In I., 5 large frogs, caught on the 21st of May, were placed in the apparatus at 9½ o'clock on the morning of the 28th. II. On the following day, at 6½ in the evening, the animals were returned to the cylinder, after having been placed in fresh water. They remained *in vacuo* until 10½ o'clock; a very small current of air was then passed through. At 8½ in the morning they were again enclosed *in vacuo* until 4 in the afternoon, and from that time until 6½ a copious current of air was admitted to them:—

	I.	II.
Weight of the animals before the experiment. .	604.195	570.537
Weight of the animals after the experiment . .	603.300	570.180
	0.895	0.357?
Carbonic acid expired	1.0865	1.9535
Carbon contained in it.	0.2964	0.5328
Watery vapour	0.7545	0.3275
Oxygen absorbed	0.9460	1.9260

Hence, as was previously found, in air which is seldom changed, the expiration of carbonic acid and the absorption of oxygen increase extraordinarily; moreover the proportion of oxygen consumed in the formation of carbonic acid and water is different; thus in I. it was = 100 : 18.48, and in II. = 100 : 35.56. The same experiment was repeated with 3 frogs which had been kept without food for a very long time; they weighed 176 grms., and evolved 0.092 grm. of carbonic acid in 24 hours. During perfect seclusion for 36 hours they yielded 0.101 grm. of carbonic acid. As the animals became very weak, and at last breathed but very little, we may also here justly conclude, that, in air which is not changed, they evolve more carbonic acid in the same time than otherwise.—*Journ. für Prakt. Chem.*, xxxvii. p. 1.

* Chem. Gaz., vol. iii. p. 162.

On Leplay's Theory of Reduction. By M. GAY-LUSSAC.

Some years ago Leplay advanced the view, that in the reduction of metals by carbon this was not the reducing agent, but the carbonic oxide. Gay-Lussac, who has gone very fully into a discussion of this theory, objects that when an easily-reducible oxide, for instance oxide of silver, oxide of copper, oxide of lead, &c., is heated with strongly-ignited lamp-black, the reduction occurs before red heat, before carbonic oxide could be formed, and that pure carbonic acid is given off. The carbon appears therefore in these instances to act directly, although it cannot be denied that carbonic oxide would reduce those metals equally well. But there are some oxides which are reduced by carbon, which cannot be reduced by carbonic oxide alone, for instance, the oxides of manganese, chromium, cerium, titanium, potassium. Now if some oxides are very easily reduced by carbon, but others which are not altered by carbonic oxide gas are likewise reduced, there is no reason to admit for the intermediate oxides that with them the carbon is perfectly inactive, and that carbonic oxide alone is capable of effecting their reduction.—*Ann. de Chim. et de Phys.*, xvii. p. 221.

ANALYTICAL CHEMISTRY.

On the Employment of the Sulphocyanide of Potassium as a Test for ascertaining the Purity of Nitric Acid. By T. KIPP.

THE extreme sensitiveness of the sulphocyanide of potassium as a test for peroxide of iron, led to its being employed for detecting iron in nitric acid. Tromsdorff however observed that sometimes a nitric acid, prepared from the purest materials, exhibited the reaction of iron. To ascertain more closely the reason of this phenomenon, the author prepared nitric acid,—1st, from ordinary *aqua regia*, freed from muriatic acid by nitrate of silver containing copper, and then slowly distilled; 2nd, according to the method described by Wackenroder; and 3rd, by employing pure sulphuric acid and pure nitre. The acid so obtained had the specific gravity 1·260–1·30; it was clear, and was not affected by sulphuretted hydrogen. A single drop of a solution of sulphocyanide of potassium gave however a more or less reddish colour to all three preparations, the weakest being the least coloured. The acids were now saturated with carbonate of ammonia, when they remained perfectly clear; and in none of them was any alteration perceptible on the addition of prussiate of potash, sulphuretted hydrogen, or sulphocyanide of potassium. Upon this the author prepared a nitric acid which contained $\frac{1}{30000}$ peroxide of iron, and treated as above. On saturation, the liquid assumed a light yellow colour, and presented a very slight trace of sediment,

Prussiate of potash coloured the suspended particles of peroxide of iron blue; sulphocyanide of potassium however did not produce the slightest alteration, although the presence of the iron had been rendered perfectly distinct by it before saturation. Rose states, in his 'Manual of Analytical Chemistry,' that the red colour which is produced by sulphocyanide of potassium in liquids containing peroxide of iron again disappears after a time on the addition of more nitric acid. In Berzelius's work we find, that when a solution of sulphocyanide of potassium is mixed with nitric acid and heated, a yellow body is formed, which has great similarity to the so-called sulphuret of cyanogen, but contains 1 equiv. sulphur more. On observing more closely the decomposing action of nitric acid upon the sulphocyanide of potassium, the author was not only able to confirm the statement of Rose, but he found, on the first addition of the acid, that the red colour of the sulphocyanide increased in intensity, and, on its slow disappearance, an evolution of gas took place, upon which the liquid assumed a light greenish tint. When the nitric acid was mixed with a little more sulphocyanide of potassium, the liquid remained almost colourless for some time; subsequently however it became red, and finally bubbles of gas were given off, upon which the liquid again exhibited a green colour. On the addition of a persalt of iron, the red colour could not be reproduced; but on the addition of a further quantity of sulphocyanide, the liquid not merely became bright red, but a violent evolution of nitrous vapours resulted, so that both the sulphocyanide of potassium and the nitric acid must have been decomposed. The author now mixed a few drops of the first hydrate of nitric acid with some water until the specific gravity was 1.07, and then added some sulphocyanide of potassium, when it immediately assumed a bright red colour. After the author had boiled a portion of the acid, he again added some sulphocyanide, but no colouring ensued. It is evident therefore that the decomposition of the sulphocyanide of potassium must have been produced by nitrous acid, which was also confirmed by the fact, that when the nitric acid had been previously freed entirely from nitrous acid by chromate of potash, peroxide of lead, &c., it required a considerable length of time before it became coloured by sulphocyanide of potassium. What the red body may be cannot yet be determined, but from the above experiments it results, that the acid must not be too concentrated for the peroxide of iron to be detected in it; that it must be in slight excess, but free from nitrous acid.—*Archiv der Pharm.*, xlv. p. 32.

On the Solubility of Alumina in Solution of Ammonia.

By M. MALAGUTI and J. DUROCHER.

It is well known that ammonia does not precipitate alumina entirely from its solutions, and that the presence of ammoniacal salts is an indispensable condition to render the precipitation complete. But hitherto it was not supposed that the portion of alumina not precipitated, on account of the absence of ammoniacal salts, might

attain very considerable proportions, especially if the solutions were dilute. Moreover, it was not known that the quantity of chloride of ammonium requisite to produce with ammonia an immediate and total precipitation of the alumina, increased in proportion as the solution was diluted with water.

The authors show that the same solution of alumina which yields with a certain quantity of ammonia twelve-thirteenths of its alumina, only parts with three-tenths if it be diluted with $3\frac{1}{2}$ times its volume of water. Moreover, the same solution of alumina which requires only 5 grms. of chloride of ammonium to deposit the whole of its alumina on the addition of ammonia, will require at least 50 grms. if it be diluted with $3\frac{1}{2}$ vols. of water.

The authors state however that their numerical results must not be regarded as absolute; for they observed that an ammoniacal solution of alumina, left to itself in a closed vessel, sometimes retains the whole of the alumina in solution, at others deposits, after a certain interval, a part or even the whole.

It is remarkable that the alumina, when spontaneously deposited from its solution, does not assume the gelatinous state like that precipitated by ammonia, but is granular. Lastly, they show, that of all the reagents employed to precipitate alumina, that which acts completely and immediately, whatever be the volume of the solution, and notwithstanding the presence of ammoniacal salts, is the hydro-sulphate of ammonia.—*Comptes Rendus*, May 18, 1846.

On a new Method of estimating Tin when this Metal is alloyed with Copper. By M. COTTEREAU.

The process is founded on the principle that copper is precipitated from its solutions by zinc before tin. The alloy of copper and tin is reduced to a fine powder, a certain quantity weighed off and digested with boiling hydrochloric acid, yielding protochloride of copper and protochloride of tin. A plate of zinc is then introduced in the hydrochloric solution of these two chlorides.

1. By a previous assay of the copper contained in the alloy by the cuprometric process of M. Pelouze the quantity of copper can be calculated, and consequently we may add to the solution of the two protochlorides an equivalent amount of zinc; or,

2. The plate of zinc may be immediately introduced into the solution of the two protochlorides, and left there until a bright iron blade does not acquire a red tint on being immersed in the liquor; the blade of zinc is then removed, and the precipitate collected on a filter.

Whichever plan be adopted, the filtered liquid is acted on just as if it were pure protochloride of tin. The protochloride of zinc formed does not in the least interfere with the reaction.—*Comptes Rendus*, June 29, 1846.

THE CHEMICAL GAZETTE.

No. XCIV.—September 15, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a second new Metal, Pelopium, contained in the Bavarian Tantalite. By Prof. H. ROSE.*

IN a former paper, on the composition of the so-called tantalic acid which occurs in the columbite of Bodenmais in Bavaria, I showed that it consisted of two acids, one of which differs so decidedly from all known metallic oxides, that I did not hesitate to regard it as the oxide of a new metal, which I named niobium†. I did not then enter into a description of the second acid, which occurs in company with the niobic acid, but merely observed that it possessed great similarity to the tantalic acid procured from the Finland tantalites.

The separation of the two acids according to the method I formerly described was exceedingly troublesome and tedious. After I had suspected a peculiar substance in the so-called tantalic acid from columbite, and had vainly attempted in various ways to isolate it, I succeeded in effecting this only approximatively on converting the acid into chloride, by mixing it with charcoal and passing a current of chlorine over the heated mixture. I obtained a yellow, readily fusible and very volatile chloride, and a white, infusible, less volatile chloride. Both were converted by water into metallic acids, which were not dissolved by the hydrochloric acid formed, but separated on boiling, and could easily be freed by washing with water from every trace of acid; but when the acid from the white infusible chloride, after I had separated it as well as possible from the yellow one, was again mixed with charcoal and treated with chlorine, I constantly obtained yellow and white chloride; less, it is true, of the first than when the mixture of the two acids as they occur in the mineral was employed; but even when the operation was very frequently repeated with the acid from the white chloride, it was not possible to obtain by this method a pure white chloride free from yellow. I observed however that the white chloride was only partially sublimed. When it was separated as much as possible from the yellow chloride, and by sublimation also from a white non-vola-

* Communicated by the Author.

† The paper here referred to will be found at p. 35 of the third volume of this Journal.

tile residue, it at last afforded an acid, which on treatment with charcoal and chlorine yielded a tolerably pure, white, wholly volatile chloride, the chloride of niobium. The white fixed residue yielded with charcoal and chlorine a large quantity of yellow chloride; and after removing this by sublimation, again left a white non-volatile residue, which, on being again subjected to a similar treatment, afforded the same products.

On comparing this behaviour of the yellow chloride with that observed on treating a mixture of pure tantalic acid and charcoal with chlorine, I obtained a perfectly similar yellow chloride and a white non-volatile residue; but the quantity was far smaller, and its production could be entirely avoided if, in the preparation of the chloride of tantalum, every trace of humidity and atmospheric air had been carefully excluded. Moreover, the sublimed yellow chloride from the Bavarian mineral very much resembled the chloride of tantalum. This similarity likewise extended to the acids prepared from the two chlorides; they behaved so much alike, that it was only after long-continued investigation properties were discovered by which they might be separated.

Both in the preparation of chloride of tantalum with the tantalic acid from the Finland tantalite, but especially in that of the yellow chloride from the Bavarian mineral, I frequently obtained considerable quantities of a red chloride, which was still more volatile than the yellow one, and proved on examination to be chloride of tungsten. When the chlorides are exposed for some time to the air, the tungsten can be removed by digestion with ammonia as readily soluble tungstate of ammonia.

Sometimes chloride of tin and chloride of titanium were obtained in preparing the chloride; they could be readily distinguished, by their fluid state of aggregation, from the other chlorides.

The formation of the chlorides of tungsten and tin was in so far remarkable, as the acids from which the chlorides were prepared had been kept in a moist condition for a long time in contact with sulphuret of ammonium. I draw especial attention to this circumstance, because, unless perfectly freed from these impurities, the chlorides and the acids prepared from them are obtained with very different properties.

The yellow chloride from the Bavarian mineral differs therefore principally from the chloride of tantalum by its leaving a white non-volatile residue on its production, or rather on its volatilization, at a high temperature. This residue consists principally of the acid which may be obtained from the yellow chloride by decomposition with water.

In the preparation of the yellow chloride from the columbite of Bodenmais, there is formed along with it an oxychloride, which is decomposed by heat into chloride and acid, just like the tungstate of the chloride of tungsten. The formation of the oxychloride can be prevented by placing a long layer of charcoal in the anterior portion of the glass tube, in which the mixture of acid and charcoal is to be treated with chlorine. While the chlorine is passing through

the tube, this charcoal is first raised to a strong red heat, and then the mixture.

The acid of the yellow chloride from the Bodenmais mineral, which is contained in it along with the niobic acid, I have named *Pelopic* acid, and the metal *Pelopium*, from Pelops the son of Tantalus and the brother of Niobe; to point out, at the same time, by this name, not only its simultaneous occurrence with the oxide of niobium, but more particularly the very great resemblance of pelopic acid to the tantalic acid from the Finland tantalites. This similarity is indeed more perfect than exists between the combinations of any other two simple metals; it is so great, that it was only after a long-continued and most minute investigation that I could decide upon publishing the results I had obtained. The combinations of niobium are, on the contrary, very different from those of pelopium or tantalium.

I will here describe the most important properties by which the compounds of tantalium differ from the corresponding compounds of pelopium, and at the same time enumerate those of niobium.

In its properties pelopic acid is intermediate between tantalic and niobic acids, just as strontia between baryta and lime. And in the same way as we are able to explain many properties of strontia, by assuming it to be a mixture of the two last-mentioned earths, we are able to determine *à priori* most of the properties of pelopic acid, by admitting it to be a mixture of a large proportion of tantalic acid with a small quantity of niobic acid; and as was the case with bromine, which, on its discovery, was considered to be a combination of chlorine and iodine, I myself was long of opinion that the pelopic acid was nothing more than tantalic acid still contaminated by a certain quantity of niobic acid, which I had not succeeded in separating. It was only by an uninterrupted investigation of this subject for several years that I became convinced of the distinctness of pelopic acid.

The chlorides of the three metals dissolve in cold concentrated sulphuric acid without any evolution of heat, but with disengagement of hydrochloric acid; but if the solution of the chloride of tantalium and pelopium is boiled, it solidifies to a jelly. Water then does not dissolve any of the tantalic acid, but a large quantity of the pelopic acid. The solution of the chloride of niobium in sulphuric acid is not rendered turbid by boiling; it even remains clear on dilution with water, but if it be now boiled, the whole of the niobic acid is precipitated from the solution.

Chloride of tantalium dissolves in hydrochloric acid in the cold to a turbid liquid, which after some length of time forms an opaline jelly, from which cold and boiling water dissolve only traces of tantalic acid. But if chloride of tantalium is treated with boiling hydrochloric acid, it does not dissolve entirely, and on cooling it does not form a jelly, but water now dissolves the whole of it to an opaline liquid, which is not rendered more turbid by boiling. Sulphuric acid produces in it, after some time, a voluminous precipitate even in the cold. The chloride of pelopium behaves in a similar manner, except that sulphuric acid does not produce a precipitate in the cold

in the solution obtained by boiling and diluted with water, but only on boiling. Chloride of niobium does not dissolve in cold hydrochloric acid; scarcely anything is dissolved on the addition of water; when however chloride of niobium is boiled with hydrochloric acid, it does not dissolve in it, but on diluting with water the whole dissolves, and the niobic acid is not even precipitated from the solution by boiling. When however sulphuric acid is added, a turbidness results even in the cold, and the whole of the niobic acid is precipitated by boiling. When, on the other hand, but a small quantity of hydrochloric acid is placed in contact with the hydrates of the acids, the result is quite a different one. The same is the case when the chlorides of the three metals are treated with much water. The niobic acid is then completely separated on boiling from the chloride of niobium, and also the pelopic acid from the chloride of pelopium; but tantalic acid does not separate quite so completely from the chloride of tantalum.

Chloride of tantalum, heated with a solution of hydrate of potash, is partly dissolved; but a solution of carbonate of potash does not dissolve any tantalic acid even on boiling. Chloride of pelopium is dissolved in large quantity by solution of caustic potash, and even carbonate of potash dissolves it in tolerable abundance on boiling. Chloride of niobium is dissolved even in the cold by a solution of potash, and also by boiling in a solution of carbonate of potash.

Tantalic acid remains white on being heated to redness; pelopic acid is rendered slightly yellowish; niobic acid, dark yellow. On cooling, both again become as white as before ignition.

All three acids exhibit, when their hydrates are heated very strongly, the phenomenon of incandescence. This however is not the case when the compounds with sulphuric acid are treated with ammonia, and then heated to redness.

Tantalic acid, exposed in a current of hydrogen to a strong red heat, remains white; pelopic and niobic acids become black; but the reduction which these acids undergo is quite inconsiderable, for very doubtful traces of water are perceptible, and the blackened acids quickly become white when heated with access of air, without experiencing any perceptible increase in weight. When tantalic acid is heated to redness in a current of gaseous ammonia in a brisk charcoal fire, it is turned gray, with the formation of but slight traces of water. Pelopic and niobic acids become black, and are reduced, with the production of a considerable quantity of water.

When tantalic acid is heated in a brisk charcoal fire, and sulphuretted hydrogen gas passed over it, it becomes slightly gray, but no trace of water is perceptible. Pelopic and niobic acids are converted by the same treatment slowly but entirely into sulphurets, with formation of water and separation of sulphur.

Metallic pelopium can be prepared from the chloride by treatment with ammonia, in the same way as the metals from the chloride of tantalum and chloride of niobium. It has the greatest resemblance to tantalum.

When the ignited acids, which are insoluble in almost all reagents

in the moist way, are fused in a silver crucible with hydrate of potash, they dissolve in it. The fused mass is soluble in water. Hydrate of soda behaves in a different manner. When the ignited acids are melted with it, the fused masses obtained are not clear; but an insoluble sediment is formed, which does not dissolve in any excess of the alkali. If the fused mass be treated with a moderate quantity of water, the excess of soda is removed, and a white insoluble mass remains. If, after removing the free soda, a large portion of water be poured over the insoluble mass, it dissolves, and most completely when niobic acid has been employed.

The insolubility of the three acids in excess of soda, while the potash compounds are soluble in excess of potash, essentially characterize them. In this they differ from similar acids, especially from tungstic acid. When the solutions of the soda salts are mixed with concentrated solutions of hydrate of soda, they immediately become turbid; if the mixture was made very slowly and carefully, all three soda salts may be obtained in crystals, which are deposited on the sides of the vessel. But crystals only of the niobate of soda can be easily obtained of any size. I succeeded in obtaining them half an inch and more in size, but in general they are much smaller. They are sparingly soluble in cold, more readily soluble in hot water; the solution may be boiled without becoming turbid; it can be evaporated, and the niobate of soda deprived of its water of crystallization without being decomposed. The salt is only rendered insoluble in water by being heated to redness.

The pelopate, and especially the tantalate of soda, are less stable; when their solutions are boiled, an insoluble white precipitate separates, which is an acid salt of soda.

When the niobate of soda is exposed to a red heat, and a current of dry sulphuretted hydrogen passed over it, a dark black crystalline mass is obtained, from which water removes hydrosulphated sulphuret of sodium, while crystalline sulphuret of niobium remains undissolved.

When pelopate of soda is treated in the same manner, there is also no sulphosalt formed, but only sulphuret of pelopium. The tantalate of soda remains white on treatment with sulphuretted hydrogen, but its soda is converted into sulphuret of hydrogen and sodium.

When niobic acid is fused with an excess of carbonate of soda until the fused mass no longer decreases in weight, the amount of oxygen in the expelled carbonic acid is twice that in the niobic acid employed. The results obtained on fusing pelopic and tantalic acids with carbonate of soda did not agree. By long-continued fusion of tantalic acid with carbonate of soda, so much carbonic acid is expelled that its amount of oxygen was equal to that of the tantalic acid employed, and finally exceeded it. But nevertheless this basic salt does not dissolve undecomposed in water, but leaves a considerable residue of acid tantalate of soda. Something similar takes place with pelopic acid, only the basic pelopate of soda formed dissolves entirely in water.

When the three acids are fused with carbonate of potash, they exhibit similar properties; but the potash salts are as soluble in the excess of carbonate of potash as in hydrate of potash. In this way we obtain compounds which are soluble in water and crystallize; but they contain carbonate of potash, which cannot be separated in any manner.

The combinations of tantalic acid with the alkalies are characterized by their passing on all occasions into insoluble acid salts, especially on boiling and evaporating their solutions. The solutions of the alkaline pelopates exhibit this property in a far less degree, those of the niobates not at all. Insoluble acid niobates of potash or soda can only be produced by not fusing the acid a sufficient time with the carbonates.

Tantallic acid is soon and entirely precipitated from its alkaline solutions by carbonic acid as an acid salt; the same is the case with pelopic acid, but with greater difficulty and far more slowly. It is owing to this that the neutral solution of tantalite of soda becomes turbid even by exposure to the air, while that of the pelopate of soda does not become turbid even after long exposure, which is characteristic of it. Carbonic acid produces a precipitate in the solution of alkaline niobate only after a considerable length of time, which however is again dissolved by much water.

When the solutions of the alkaline tantalates and pelopates are treated with an excess of hydrochloric acid, the eliminated acids dissolve to faintly opaline liquids. Sulphuric acid produces in these solutions precipitates, and separates the acids on boiling; however, only the pelopic acid entirely, and not so the tantalic acid. Hydrochloric acid precipitates the acid from the solutions of the alkaline niobates in the cold, and still more so on boiling; an excess of hydrochloric acid merely dissolves slight traces. This behaviour is in so far interesting, as we have seen that under other circumstances niobic acid may be wholly soluble in hydrochloric acid. Sulphuric acid precipitates niobic acid from its alkaline solutions even in the cold.

From the solutions of the alkaline tantalates the acid is entirely precipitated, without the assistance of heat, by chloride of ammonium, pelopic acid less perfectly, and niobic acid still less.

When the solutions of the alkaline tantalates are rendered acid with hydrochloric or sulphuric acid, a pale yellow precipitate is produced in them by tincture of galls. An orange-yellow precipitate is formed, under similar circumstances, in solutions of the pelopates, and a dark orange-red in those of the niobates.

Ferrocyanide of potassium produces in solutions of the tantalates of the alkalies, when they have been rendered slightly acid, a yellow precipitate; in those of the pelopates, a brownish-red; and in those of the niobates, a red one.

When the three acids are fused with bisulphate of potash, they dissolve in it. Niobic acid alone solidifies with it to a crystalline mass. Water removes sulphate of potash from the fused masses, and leaves compounds of sulphuric acid with the metallic acids,

from which however the sulphuric acid can be removed by very long treatment with water.

When hydrochloric or sulphuric acid is added to the solution of the niobate of potash or soda, and then a bar of zinc immersed in it, the separated niobic acid soon assumes a very beautiful pure blue colour. It gradually becomes dirtier, and finally brown. The blue colour is produced, in the solutions of the alkaline pelopates, only on the addition of sulphuric acid; but not even then is a blue colour produced in the alkaline tantalates, which however takes place when the solution of the chloride of tantalum in sulphuric acid is treated with water and zinc.

Tantalalic acid yields before the blowpipe colourless pearls with the fluxes even in the inner flame; pelopie acid gives with the microcosmic salt in the outer flame a colourless, in the inner one a brown pearl. Niobic acid colours the microcosmic salt in the inner flame of a beautiful blue; the pearl can be easily blown colourless in the outer flame.

These are the most important differences between pelopie acid and tantalalic acid on the one hand, and niobic acid on the other. To ascertain accurately the behaviour of these acids and their combinations is one of the most difficult tasks, as all three acids frequently exhibit highly anomalous properties. We have seen, for instance, that the niobic acid is readily dissolved, under certain circumstances, by hydrochloric acid, when separated from its combinations, while under not very dissimilar circumstances it is almost entirely precipitated by it. This is owing to the acid assuming different isomeric modifications.

The three acids resemble in this respect silicic acid, the behaviour of which towards reagents is frequently remarkable, and only excites less surprise from our having been long acquainted with this acid, and its properties having been thoroughly examined.

This tendency of the three acids to assume different isomeric modifications is connected with the great variability which they exhibit with respect to their specific gravity. My experiments on this subject have led me to the most unexpected results; although I have not terminated my investigations, I will nevertheless communicate at present some of the most important.

Some time ago I drew attention to the fact, that in the artificially prepared titanitic acid the specific gravity gradually increases by long-continued ignition, until it attains that of rutile. In the same way the modifications of titanitic acid which occur in nature, anatase and brookite, may be converted by continued ignition into rutile. I thought that the publication of these facts would have induced chemists to examine the specific gravity of other oxides at different temperatures, since these changes have an important influence on the atomic volume. This however has not happened, with the exception of a very interesting investigation of Count Schafgotsch, on the specific gravity of silicic acid, in which he has shown that opal heated to redness has so low a specific gravity, that it floats on oil of vitriol; but that the specific gravity is so increased by heating to

redness, that it equals that of chemically-prepared silicic acid (2.2), but which is still considerably lighter than quartz and rock-crystal (2.6).

The changes which the three metallic acids under consideration experience by heating to redness are far more remarkable. When the hydrate of pelopie acid is deprived of its water by a gentle red heat over a spirit-lamp, just sufficient to produce the phenomenon of incandescence, and then exposed to a strong red heat in a charcoal fire, its specific gravity is considerably increased. If we examine the ignited acid under the microscope, we see that it consists for the greater part of amorphous granules, in which some small crystals are perceptible. The ignited acid was then exposed to the most intense, and at the same time continuous heat that a platinum crucible is capable of bearing, that of the porcelain furnace of the Royal Berlin Manufactory. The acid was not melted by it, but was converted into a coarse sandy powder, which, examined under the microscope, consisted of large perfect crystals. The specific gravity of the acid however was thereby considerably diminished; curious enough, it had become still lower than that which the acid possessed after the hydrate had been exposed to a gentle heat over a spirit-lamp in order to expel its water.

On repeating this experiment, the specific gravity of the crystallized acid, which had been ignited in the porcelain furnace, was found to be constant, while by no other temperature could the acid be brought to a constant specific gravity.

These experiments are in so far remarkable as they prove precisely the contrary of what has hitherto been frequently admitted. Crystalline bodies, such as vesuvian, epidote and garnet, fuse at a high temperature, become amorphous, but of lower specific gravity. It is evident that what applies to these substances cannot be advanced as a general rule.

Niobic acid has a far lower specific gravity than pelopie acid. It exhibits a similar behaviour. The acid, exposed to the temperature of the porcelain furnace, appears under the microscope perfectly crystalline.

Tantalie acid behaves very different to the other two acids. It is the heaviest of all, and, by heating to redness in a charcoal fire, increases considerably in specific gravity, from 7.0 or 7.1 to 8.2. In the fire of the porcelain furnace it is likewise converted into a coarse powder, but which does not appear distinctly crystalline under the microscope. Its specific gravity is thereby only slightly lessened.

In all these experiments no alteration in the absolute weight was perceptible.

Poisoning with Fly-Powder. By Dr. DE SCHOBENS.

Among those causes of poisoning which are not the result of crime, but of negligence or ignorance, fly-powder is a very frequent one. People are surprised to learn that this powder contains arsenic, and that it can kill men as well as flies; and hence the carelessness

with which it is exposed within the reach of children and others. That which is generally employed comes from the cobalt mine of Tunaberg, and is composed of cobalt, arsenic, iron and sulphur. A few years ago the author was called to attend a man who had swallowed a quantity by mistake for a purgative; he was soon attacked with all the usual symptoms of poisoning with arsenic; but not supposing that the poison for flies would be also poison for him, he took no remedy but a large quantity of milk, which he vomited immediately. Fifteen hours after he had swallowed the poison Dr. S. was called to see him; but he found the patient to be then too far gone for antidotal treatment to be of any avail. Stimulants and lime water were ordered, but the necessary medicines had scarcely been sent for when the patient died. The second case occurred recently in a child, *ætat.* 4. Dr. S. was sent for immediately that the child took ill; and finding what had been taken, he at once ordered a dessert spoonful of the hydrated sesquioxide of iron to be given every half hour. The symptoms became gradually ameliorated, and the following day the child, though weak, was almost well.—*Encyclo-graphie Méd.*, May 1846; and *Monthly Journ. of Med. Science*, Sept. 1846.

Chemical Examination of Goose-fat and Oleic Acid.

By Dr. J. GOTTLIEB.

Goose-fat yields, on dry distillation, acroleine; there is no doubt therefore that, like all the ordinary fats, it contains glycerine. Several pounds of goose-fat were boiled with caustic potash to a clear jelly, and then distilled with an excess of sulphuric acid, a turbid, faintly-acid water passed over, which was neutralized with hydrate of lime and evaporated. The acid combined with the lime, on separation by a mineral acid, possessed all the properties of a mixture of the volatile acids contained in butter, and the odour of butyric and caproic acids were particularly perceptible. From the small quantity, it could not be ascertained whether capric and caprylic acids were likewise present. The acids in the retort were pressed between paper after solidification, and in this way the greater part of the oleic acid removed. The residuary solid acids were repeatedly dissolved in spirit, and freed by crystallization and pressure from the still-adherent oleic acid; they then formed a brilliant white shining mass, which solidified on cooling to a crystalline mass, whose melting-point was 136° F. This could not be altered even by repeated recrystallization from larger quantities of spirit than usually employed for this purpose. This substance is therefore a mixture of stearic and margaric acids, the separation and purification of which are attended with some difficulty, and always require for success considerable quantities of the mixture. To separate the stearic acid, the first portions which crystallize from a hot alcoholic solution on incipient cooling are employed. By repeated solution and separation of the portion which first crystallizes, the stearic acid is at last obtained pure. In this manner the author prepared pure stearic

acid from goose-fat, the melting-point and other properties of which agreed perfectly with those already known; moreover, the identity of this acid with stearic acid was proved by analysis, which led to the formula $C^{68}H^{66}O^5 + 2HO$.

When the mother-ley, from which the greater portion of the stearic acid has separated on the cooling of the alcoholic solution of the mixed acids, is set aside at the ordinary temperature, some impure crystals of margaric acid at first separate, and subsequently pure crystals in porcelaneous masses. By frequent recrystallization and careful removal of the first portions, pure hydrated margaric acid can be obtained from the mixture. It possessed all the known properties of margaric acid, and yielded on analysis the formula $C^{34}H^{33}O^5 + HO$.

With respect to the melting-point of a mixture of the two acids, they stand in the same relation as certain metals, whose alloys fuse at a far lower temperature than the metals themselves. As this property might lead to errors in a careless examination of either of the acids, and at the same time the melting-points in mixtures allow of a tolerably accurate conclusion as to the proportions of the mixed acids, the author made some experiments to determine the melting-point of mixtures of the two acids in known proportions with the following results:—

Stearic acid.	Margaric acid.	Melting-point.	Stearic acid.	Margaric acid.	Melting-point.
I. 30 parts to 10 parts.		150° F.	VI. 10 parts to 15 parts.		135° F.
II. 25 ... 10 ...		149 ...	VII. 10 ... 20 ...		134 ...
III. 20 ... 10 ...		147 ...	VIII. 10 ... 25 ...		131 ...
IV. 15 ... 10 ...		142 ...	IX. 10 ... 30 ...		133 ...
V. 10 ... 10 ...		137 ...			

The solidified stearic and margaric acids are perfectly crystalline; the first forms confused masses of small, the latter large, shining, acicular crystals; the mixture V. is far less crystalline; VI. nearly resembling porcelain, opaque and very brittle, so that it sometimes cracks on cooling; VII. is dull and opaque; but VIII. and IX., in which the margaric acid already preponderates to a considerable degree, again exhibit a crystalline and shining appearance. The same applies to I. and II.; while III. and IV. already approach closely to V. As far as our knowledge goes of the solid fatty acids, it may generally be assumed as correct, that pure acids nearly always exhibit a shining crystalline appearance immediately on solidification after melting; while mixtures of several of these acids present a turbid dull surface, with scarcely any lustre.

Oleic Acid.—Chevreul describes his oleic acid as a colourless oil, of slightly rancid taste and odour, and strong acid reaction. It solidified some degrees below 32° F. to a white crystalline mass. The mode of preparation adopted by Chevreul rendered it possible that it might be contaminated with a small quantity of margaric acid. He arrived, by his analyses of oleic acid, at the formula $C^{70}H^{58}O^5 + 2HO$. Varrentrapp prepared his oleic acid by separating the oleate of lead from the margarate and stearate of lead by solution

in æther. Varrentrapp's acid was slightly yellow and of acid reaction; on analysis he found $C^{44}H^{30}O^4 + HO$. The oleic acid, obtained by Dr. Bromeis from butter, likewise from the lead salt, had a strong yellow colour, which could be removed by animal charcoal, which proves that the acid prepared in this manner contains some foreign colouring substance, which can be separated without decomposing the oleic acid. The formula advanced by Bromeis is $C^{34}H^{30}O^4 + HO$. This great difference in the results of the investigations, and also the circumstance that oleic acid constantly absorbs oxygen, rendered it probable that the oleic acids hitherto examined were mixtures of the substance with its products of oxidation, which are already partially formed in the organism of the animal or plant. To arrive therefore at a correct result, the experiments should be so performed that the substances in question remain protected from the access of air, especially at a temperature above 53° , as much as possible. They must be dried, therefore, according to circumstances, either in a current of carbonic acid or *in vacuo*; but the weighing off of the hydrated oleic acid for the purpose of analysis should be accomplished at a low temperature. To obtain pure oleic acid, crude acid is taken, by which is meant that separated from all the solid acids by means of oxide of lead and æther. This contains, whether procured from almond-oil, olive-oil, goose-fat or butter, along with the pure oleic acid, products resulting from its oxidation, and also a brown colouring substance. A large excess of solution of ammonia is added to it to prevent the formation of acid salts, and it is then precipitated with chloride of barium. Oleate of barytes is precipitated, which is dried and boiled with moderately strong alcohol. In this operation the salt melts to a transparent tenacious fluid, on which account the digestion must be carried on with care. In this way a portion of the pure oleate of barytes contained in the mixture is dissolved, and falls, on the cooling of the filtered alcoholic solution, in minute crystalline scales. This is repeated with fresh quantities of spirit, and the collected barytes salt recrystallized once or twice from alcohol, when it forms a brilliant white, loose, finely-crystalline powder, which does not melt at 212° , but only cakes slightly together. The oleate of barytes is now decomposed with tartaric acid, and the separated acid freed by washing with water from adherent tartaric acid. A second method of preparing pure oleic acid, which can sometimes be readily and easily employed, is as follows:—When crude oleic acid is exposed to a temperature of 21° – 19° F., it solidifies to a crystalline mass of greater or less consistence. Pure oleic acid alone possesses the property of solidifying, its products of oxidation remaining liquid at this temperature. The greater portion of the fluid smeary mass inclosed in the crystals of oleic acid must first be removed by pressing the solidified acid between blotting-paper. It is not advisable to effect this in a press, even though it may have a temperature sufficiently low for the purpose, as the fluid portion, from its smeary nature, is not well absorbed by the paper, and it consequently requires longer time for a

large quantity of acid than when small portions are successively treated one after the other. The acid is then placed in a warm situation, and immediately after it has melted again allowed to solidify. After frequent pressure the acid becomes whiter and possesses greater lustre, so that it exhibits in the solid state great resemblance to stearic acid which has crystallized from alcohol. To remove now the last traces of the fluid and coloured portion, a little alcohol is added to it, and it is again exposed to the cold, when it crystallizes in beautiful dazzling white needles, and is again submitted to pressure. This proceeding is continued until the acid, when dried in a current of carbonic acid, presents a melting-point of 57° , which is that of pure oleic acid. This mode of preparation of oleic acid can however only be employed when the crude oleic acid is not contaminated to too great an extent, either from long preservation, or by a process of oxidation in the organism itself with the above-mentioned substances, which do not become solid at 21° , as they prevent the crystallization of the oleic acid. The oleic acid, prepared according to either of the above methods, above 57° , is a perfectly limpid colourless liquid, of oily consistence, possessing neither odour nor taste, and not reddening blue litmus-paper even when dissolved in spirit. At about 40° it solidifies, and forms a perfectly white crystalline mass, which at the moment of solidification contracts considerably, whereby the still-fluid portion is pressed out over the surface; it is then very hard. It cannot be distilled unaltered, and in the solid state absorbs no oxygen; but when liquid it is readily and rapidly oxidized. The analysis of this substance yielded the following results:—

	I.	II.	III.	IV.			
Carbon.....	76.51	76.37	76.12	76.34	36 =	2700	76.59
Hydrogen....	12.12	12.09	12.16	12.20	34	425	12.06
Oxygen	11.37	11.54	11.72	11.46	4	400	11.35

I. II. III. were prepared from olive-oil, IV. from goose-fat.

In the preparation of the oleates, the chief thing is to prevent the formation of acid and basic salts, which readily occurs. For this purpose pure oleic acid was dissolved in absolute alcohol, and then an excess of dry carbonate of soda added, applying at first a gentle heat, and subsequently boiling, until the liquid acquired a distinctly-alkaline reaction. The solution of the neutral soda salt is separated from the carbonate of soda by rapid filtration, and immediately diluted with a sufficient quantity of water, upon which the whole is allowed to cool, well covered. This is important, because otherwise a precipitate is obtained which cakes together and is difficult to wash. Neutral acetate of lead is added to the cold solution; the oleate, which falls as a white flocculent precipitate, is quickly separated by filtration in a cool place. The oleate of lead, dried *in vacuo*, forms a light, loose, white powder, which melts at about 176° to a yellow liquid that on cooling becomes brittle and transparent. Its composition is—

Carbon	56.03	55.73	36 =	2700.0	56.16
Hydrogen	8.67	8.70	33	412.5	8.58
Oxygen	6.35	6.62	3	300.0	6.25
Oxide of lead ..	28.95	28.95	1	1394.5	29.01

The above salt was prepared with oleic acid from olive oil. The oleate of barytes above described gave—

	I.	II.			
Carbon	61.68	61.34	36 =	2700.0	61.79
Hydrogen	9.46	9.41	33	412.5	9.44
Oxygen	6.67	7.59	3	300.0	6.87
Barytes	22.19	21.66	1	956.9	21.90

I. was prepared from butter, and II. from oil of almonds.

From these facts, the formula $C^{36}H^{33}O^3 + HO$ results for pure hydrated oleic acid.

The impurities of the oleic acid, in the treatment of the crude oleate of barytes with alcohol, remain combined with barytes dissolved in the liquid. On evaporation, a brown smeary mass, of a disagreeable odour, is obtained. A strong mineral acid separates from this a reddish-brown tenacious oily liquid, of a rancid odour and taste, and having a strongly acid reaction. The compound contains 14.28–15.63 per cent. baryta.

[To be continued.]

On the Presence of Lead, Copper and Arsenic in certain kinds of Paper, and the Chemical Processes necessary to discover such Impurities.

Government having been informed that sulphate of lead was used in the manufacture of the pulp for certain kinds of paper, caused the paper to be seized, and required a chemical examination of it. The experiments were conducted by MM. Payen and Chevallier, and they found that the paper contained $4\frac{1}{2}$ per cent. of the salt.

In order to ascertain the weight of the sulphate of lead, it was separated in the following manner:—The paper was incinerated, and the ashes obtained were mixed with carbonate of soda; this mixture was then boiled for three-quarters of an hour, in order to convert the salt into carbonate of lead; the insoluble matter was then collected upon a filter, washed with distilled water, and treated with diluted acid. When the carbonate was dissolved, a stream of sulphuretted hydrogen gas was passed through the acidulated fluid, in order to convert the lead into a sulphuret; the sulphuret was then collected, washed, and by nitric acid converted into sulphate; and lastly, the weight of the salt determined. It was ascertained that the paper contained sulphate of lead by moistening it with hydrosulphuric acid, when it showed the usual dark stain, the coloration being deeper in proportion to the quantity of lead which the paper contained.

The hydrosulphuret of ammonia must not be employed for this purpose, because this reagent communicates a dark stain to paper

containing salts of iron, or in the manufacture of which sulphate of alumina has been employed, as this salt frequently contains iron.

Copper, arsenic and lead are present in paper in consequence of the *débris* of coloured papers, scraps which owe their colour to salts of arsenic and copper, cards called porcelain, and papers coloured with red lead, all entering into the composition of the pulp used for the manufacture of paper.

The presence of copper was recognised by minutely dividing the paper, and placing it in contact with pure ammonia; the copper is dissolved, and may be obtained on evaporation. To show the presence of arsenic, the paper was carbonized by sulphuric acid; the carbonized mass was mixed with water, and introduced into Marsh's apparatus.

It is conceived that the quantity of lead, copper and arsenic contained in the paper manufactured for wrapping up articles of merchandise is very minute; but it is equally interesting with regard to public hygiene, as well as to medico-legal researches, that we should be aware that these poisonous agents do exist in paper in various proportions.—*Gazette Médicale de Paris*, June 1846; and *Monthly Journ. of Med. Science*, Sept. 1846.

On Dumasine. By M. HEINTZ.

As is well known, Kane has described under this name an oily product, which is formed at the same time with acetone in the distillation of acetate of lime, and assigned to it the formula $C^{10}H^8O$, according to which it would be isomeric with camphor. As the origin of this body cannot be well explained, and moreover Kane employed an acetate of lime prepared with wood-vinegar, so that empyreumatic substances may have passed from the wood-vinegar into the product, Heintz has submitted the empyreumatic substance obtained on distilling 2 parts of sugar of lead with 1 part lime to further examination. The purified product was composed according to the formula C^6H^5O , which is identical with that for Kane's mesitic æther (oxide of cœnyle according to Berzelius), with which it also perfectly agreed in its properties. No compound corresponding to the formula for dumasine could be detected.—*Poggendorff's Annalen*, 1846, No. vi.

Determination of the Sulphur in the Nitrogenous Constituents of Vegetable and Animal Bodies. By Dr. E. RÜLING, Dr. WALTHER, F. VERDEIL and A. SCHLIEPER.

In the last number of this Journal we gave an account of Laszkowski's objections to Mulder's theory of proteine, in which the importance of ascertaining with the greatest accuracy the amount of sulphur contained in the so-called proteine compounds was insisted on. The number of Liebig's Journal for July already furnishes us with numerous determinations made by several chemists in the Giessen laboratory, the results of which are contained in the following

table. The mode of determining the sulphur was by fusing the finely-pulverized substance in a spacious silver dish, with about 12 times its weight of caustic potash perfectly free from sulphuric acid, then mixing it with pure nitre in weight equal to about half the potash employed, and heating it until the fused mass appeared perfectly white. The whole was then dissolved in distilled water, supersaturated with hydrochloric acid, and the sulphuric acid precipitated by a salt of baryta.

<i>Legumine.</i>	Per-centage of sulphur.	<i>Fibrine.</i>	Per-centage of sulphur.
1. From peas	0.505	1. From a mixture of arterial and venous ox-blood	1.319
2. From peas,—having been previously dissolved in solu- tion of ammonia	0.467	2. From ox-blood*.....	1.593
3. From beans	0.557	<i>Crystalline Lens.</i>	
4. From beans,—having been previously dissolved in solu- tion of ammonia	0.445	1. Mixture of that from oxen, calves and pigs.....	1.003
<i>Vegetable Albumen.</i>		2. From oxen.....	1.121
1. From peas	0.790	3. From a calf	1.233
2. From potatoes	0.969	<i>Albuminose*.</i>	
<i>Gluten.</i>		1. Prepared according to Bou- chardat's method	1.599
1. From wheat-flour	1.134	2. Ditto	1.441
2. From rye-flour*.....	0.989	<i>Isinglass.</i>	
3. Ditto*	0.972	1. Washed with alcohol and æther*	0.727
<i>Caseine.</i>		2. Ditto*	0.647
1. From cow's milk	1.016	3. Ditto†	0.560
2. From cow's milk,—dissolved in a tolerably strong solu- tion of carb. soda.....	0.850	<i>Crystalline.</i>	
3. Ditto†	0.933	1. From a mixture of the cry- stalline lenses of oxen, calves and pigs	1.103
4. Ditto*	0.843	2. From oxen.....	1.227
<i>Albumen.</i>		<i>Pig's Bladder*.</i>	
1. From eggs	1.748	1. Purified by washing with water and alcohol.....	1.263
2. Ditto*	2.109	2. Ditto	1.354
3. From the serum of a mixture of arterial and venous ox- blood.....	1.386	<i>Cartilage*.</i>	
4. From serum of arterial horse's blood	303	Of a person who had com- mitted suicide, ætat. 50 ...	0.652
5. From serum of venous horse's blood.....	1.285		

Those numbers to which an * is affixed were obtained by Dr. Verdeil, those with † by Dr. Walther, those with ‡ by A. Schlieper, and those without any mark were found by Dr. Rüling, who also determined the amount of carbon and hydrogen of the substances examined by burning with chromate of lead. As his results do not

differ from those generally received, except in the case of legumine, which agreed better with those found by Dumas and Cahours than with those obtained by Mulder and Rochleder, we have not considered it necessary, with this exception, to give the numbers. Dr. Rüling found in 100 parts of legumine, dried at 212°—

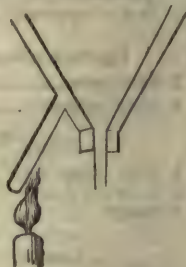
					Mean.
Carbon.....	50.68	50.51	..	..	50.59
Hydrogen ..	6.74	6.93	..	..	6.83
Nitrogen	..	..	16.50	16.58	16.54
Oxygen	..	..	..	..	25.57
Sulphur	..	..	..	..	0.47

Description of a Water-bath Funnel for filtering hot Solutions.

By M. PLANTAMOUR.

To filter boiling-hot saturated solutions without the dissolved substance crystallizing during filtration on the filter, it is usual to fit the funnel into a larger tin funnel by means of a perforated cork for the reception of the neck of the inner funnel, and to fill the interval between the two with boiling water. The water however soon cools, and must be often renewed.

M. Plantamour has essentially improved the apparatus in a very simple manner, by soldering to the side of the tin funnel, as represented in the annexed figure, a lateral tube having a downward direction, and which is closed at the bottom. This can be heated with a spirit-lamp, and the water in the funnel thus kept boiling.—Poggendorf's *Annalen*, 1846, No. iii.



On Turpentine-camphor. By M. WIGGERS.

The author has communicated some experiments on turpentine-camphor, the best proportions for obtaining which in large quantities he found to be 8 parts oil of turpentine, 2 nitric acid of 1.25 to 1.3 spec. grav., and 1 part alcohol of 0.863 spec. grav. This mixture is frequently shaken for some days until, on being set aside at 68°–78°, the camphor separates from the liquid. Turpentine-camphor is only formed from that modification of the oil of turpentine which yields a crystalline compound with muriatic acid; and no camphor could be procured from an oil which could not be combined with muriatic acid. Sulphuric, muriatic and acetic acids act in precisely the same manner as nitric acid.

The camphor obtained, according to this process, is slightly coloured; it is purified by recrystallization, for which purpose it is dissolved in boiling water. The analysis of this pure camphor proved it to be a hydrate of the oil of turpentine corresponding to the formula $C^{20}H^{16}6aq$.:—

Carbon	63·31	20	63·21
Hydrogen	11·55	22	11·55
Oxygen	..	6	25·24

When this body is heated to melting, it loses 2 equiv. water, and the fused body thus obtained is $C^{20}H^{16} + 4aq$.

If either of these two hydrates be placed in a vessel, and a current of dry muriatic gas be passed into it, the camphor becomes liquid, disengages heat, and two colourless layers are obtained; the lower one is muriatic acid, formed from the water of the camphor; the upper one is of an oily consistence, and is a combination of oil of turpentine with muriatic acid, $C^{20}H^{16}HCl$.

On treating turpentine-camphor with hydriodic acid, an analogous compound was not formed, but the hydrate of the oil of turpentine with 1 equiv. water. The bodies examined are therefore combinations of oil of turpentine with 1, 4 and 6 equivs. water, and with 1 equiv. muriatic acid.—*Ann. der Chem. und Pharm.*, Feb. 1846.

On the Action of Nitric Acid upon Cholic Acid. By A. SCHLIEFER.

The interesting connexion which has recently been shown to exist between the products of decomposition of cholesterine and choloidic acid by Prof. Redtenbacher*, led to the supposition that it might also extend to the other products of the bile if they were submitted to a similar treatment. With this view I have been induced to examine the action of nitric acid on Demareay's cholic acid.

The cholic acid was prepared according to the process described by Theyer and Schlosser; bile, freed from mucus, fat and colouring substance, was retained for several days at a boiling temperature with a tolerably strong solution of potash, and then concentrated until a soapy mass, which became hard on cooling, separated from the liquid. After complete separation, it was dissolved in water, filtered, and treated with acetic acid, which separates the impure cholic acid in thick white flakes, which unite, forming resinous masses. If the eliminated resin be heated with water to boiling, it assumes all at once a granular crystalline structure, and is then easily reduced to powder; the latter was dried, and washed on a funnel with æther until it appeared white, and then pure white cholic acid obtained from it by dissolving and crystallizing it from alcohol. Cholic and nitric acids do not act on one another in the cold, however concentrated the latter may be; but if a mixture of the two be heated in a retort, a very violent reaction soon ensues, the mass ascends, frothing considerably, while large quantities of nitrous acid escape. When the first action is over, the retort contains a dark yellow liquid, on which float some drops of oil, which on cooling solidify, and are nothing more than unaltered cholic acid. As the nitric acid which distilled over possessed a peculiar odour, it was nearly saturated with an alkali and again distilled; but although the aqueous distillate still retained the peculiar smell,

* *Chem. Gaz.*, vol. iv. p. 269.

none of the volatile products which Redtenbacher discovered in submitting cholesterine and choloidic acid to a similar treatment, could be detected in it. The yellowish liquid which remained in the retort was evaporated on the water-bath to expel the excess of nitric acid, when it dried to a yellowish transparent gum, which exhibited in its external properties the greatest resemblance to the cholesteric acid recently described by Redtenbacher. To separate this body from some still undecomposed cholic acid, it was repeatedly dissolved in water, filtered, and again evaporated until the residue dissolved to a clear solution in water. To ascertain the presence of cholesteric acid, the silver salt was prepared by dissolving the acid gummy mass in water, neutralizing with ammonia, and precipitating with nitrate of silver; it was deposited in thick white flakes. Oxalic acid was not present. To obtain the silver salt in a crystalline state, some nitrate of ammonia was added to the mother-ley from which it had been precipitated, in order to increase the solubility of the silver salt in it, then boiled with the precipitate, when the greater portion dissolved; on cooling, the cholesterate of silver separated from the hot filtered liquid, on the bottom and sides of the glass, in granular crystalline yellowish crusts; more of the salt was obtained by evaporating the mother-ley. The salt, dried at 212° , yielded 57.69 oxide of silver, 23.81 carbon, and 2.35 per cent. hydrogen; leading to the formula $\text{AgO}, \text{C}^3 \text{H}^4 \text{O}^4$, which is that of the cholesterate of silver.

The contemporaneous occurrence of cholesteric acid in the products of decomposition of choloidic acid, cholesterine and cholic acid by nitric acid exhibits the close relationship of these three bodies as respects their constitution.—Liebig's *Annalen*, lviii. p. 375.

On the so-called Gold, Silver and Copper Bronzes.

By R. BÖTTGER.

Genuine copper bronze, such as is employed for colour-printing in lithography, consists of pure copper; genuine silver bronze, of pure silver; the spurious, of powdered tin. The dearest kind of gold bronze consists of pure gold; that usually employed for printing in gold is a kind of brass powder; another kind is the sulphuret of tin. The genuine silver and copper bronzes are best adapted for bronzing casts for galvano-plastic purposes, for which the spurious gold bronze is wholly unsuited.—*Vorles. über Chem. und Phys.*

ANALYTICAL CHEMISTRY.

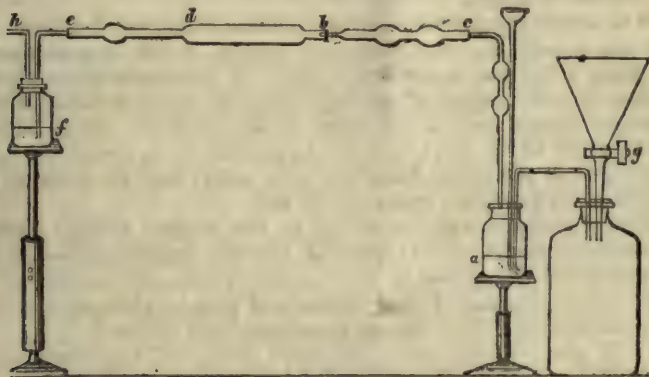
On the Determination of Carbonic Acid in Saline Compounds.

By C. BRUNNER, Sen.

THE estimation of carbonic acid in its combinations is generally effected by ignition, when the compound is one of those which part with the whole of the acid at a red heat. When water is disengaged

at the same time, its quantity must either be determined by a separate experiment, and subtracted from the loss experienced on ignition, or collected in a suitable apparatus during the calcination, and so calculated. With those compounds where this method cannot be applied, it is customary to expel the carbonic acid by a stronger acid, for instance sulphuric acid, and to determine its amount from the loss, taking care in this case to retain the water accidentally carried over with it by some suitable substance. Apparatus for this mode of determination have been described by Rose, and recently by Fresenius.

It is readily seen that, according to these methods, the result is always obtained in a negative manner, that is to say, by a loss in weight. As we should certainly endeavour to exchange all such negative methods for positive, I will here communicate one which appears to me applicable in most cases. The substance to be examined is placed in the little flask *a*, and a suitable quantity, for



instance an ounce, of water poured over it; upon which the flask is closed with a tight-fitting cork provided with three tubes, and when necessary coated with cement. The straight tube terminates above in a small funnel, through which the sulphuric acid is poured; the second, provided with two bulbs, is connected by its rectangular bend with a tube *bc*, from a third to half an inch wide; and, in order to gain space, likewise furnished with two expansions containing asbestos moistened with sulphuric acid; the third is bent twice, and terminates in the large empty flask. To adapt it more easily, it may be cut anywhere in the middle, and the two parts connected by caoutchouc. The two tubes dipping in the liquid *a* are drawn out at their lower ends into fine, somewhat laterally curved points; the tube *bc* contains, in the expanded portion *bd*, which is from three-quarters to an inch in width, well-burnt lime, which may be readily moistened with water, from *d* to *e*, asbestos, or fragments of pumice-stone, drenched with sulphuric acid, and separated from the lime by a light stopper of asbestos; the small Woulf's flask contains lime-water.

The analysis is now performed in the following manner:—A small quantity of sulphuric acid is poured into the flask *a* through the funnel-tube, the stopcock *g* being closed; as this will not descend of itself, it is made to do so by drawing gently with the mouth at *h*. The evolution of gas, which is rendered perceptible by the ascending bubbles, and by the air passing through the lime-water in *f*, is now waited for; another portion of acid is then added, and this continued until it may be assumed that a tolerable excess of acid has been introduced. This being done, some water containing a little caustic potash in solution is allowed to flow into the flask by opening the stopcock *g*, whereby a current of air is passed through the vessel *a*, which carries the carbonic acid, contained partly in the liquid partly in the upper space of the vessel, into the tube *be*; but since this would never be completely effected without the application of heat, the vessel *a* towards the end of the experiment is immersed in a small dish filled with water, which is kept warm over a small lamp as long as is found requisite.

It is best to regulate the current of air so that about 2 bubbles of gas pass through the lime-water in a second. It will however never be found to become in the least turbid. It is scarcely necessary to observe that the object of the sulphuric acid in *bc* is to retain the moisture carried by the gas from *a*; also that the potash added to the water which flows into the large flask is to absorb the carbonic acid of the atmospheric air; and, lastly, that, the increase in weight of *be* yields the result sought for.

Several analyses made according to this method yielded highly satisfactory results. 1.771 grm. of recently ignited carbonate of potash, which was allowed to cool in a closed platinum crucible, gave 0.564 carbonic acid. Taking the atom of potash at 590, that of the carbonic acid at 275, 0.563 ought to have been obtained.

1.705 grm. of very pure magnesite gave 0.870 carbonic acid = 51.026 per cent.—Poggendorff's *Annalen*, No. vi. 1846.

On the Employment of Guaiacum-resin as a Test. By G. OSANN.

According to Schönbein, guaiacum-resin is coloured blue by ozone; the same alteration is also effected by chlorine. This circumstance can be turned to account for detecting very feeble electric currents, by passing them through a mixture of a few drops of tincture of guaiacum and common salt. The guaiacum solution however should always be recently prepared.

The solution of guaiacum is extremely sensitive towards perchloride of iron, so that when present in so small a proportion as not to act upon tincture of galls, it still colours the solution of guaiacum blue.—Poggendorff's *Annalen*, lxvii. p. 372.

THE CHEMICAL GAZETTE.

No. XCV.—October 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on the Theory of Proteine.
By GEO. KEMP, M.D., Cantab., F.C.P.S.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

THE subject of proteine is so important in its relations to animal and vegetable chemistry, that any analytical researches which have a tendency to render its nature more intelligible, or to correct any previous misapprehensions respecting it, must be considered as of paramount importance. The recent researches of M. Laskowski (published in the 'Chemical Gazette, No. xciii.) are calculated to convey an impression, to the minds of those whose engagements may not permit them minutely to investigate the subject, that the very groundwork on which important conclusions have been conventionally received by all parties is unsound, and that the whole fabric of organic chemistry in its relations to physiology must be again surveyed and remodelled. With the full conviction that no apology is necessary for the introduction of even preliminary investigations on the subject, the writer begs attention to the following facts, at once to a great extent confirmatory of M. Laskowski's qualitative analyses; whilst, at the same time, tending to show that, with the full admission of their truth, the deductions of Prof. Mulder remain practically unaffected.

The problem to be solved is, Does the proteine of Mulder contain sulphur; and, if so, does it contain sufficient to affect conclusions resulting from the adoption of his formula, or indeed any other legitimate empirical expression for its composition? If we take perfectly fresh albumen, treat it with hydrochloric acid, and then into the filtered solution pass a current of chlorine gas, we obtain a copious white precipitate, which can be collected and washed without difficulty (Berzelius, vol. ix. p. 813). This body is denominated chlorite of proteine, from its being a compound of what Mulder denominates proteine and chlorous acid. Now it is assumed that this body, easily prepared and isolated, affords a legitimate subject upon which to found a decision, that if sulphur be contained in this body the same element must be admitted to exist in proteine, and that the

quantity contained in it will determine the quantity contained in
proteine.

In order to render the conditions of the analyses similar, the method used by Prof. Redtenbacher for the determination of the sulphur in taurine was adopted in this case; not however because the writer believes that method the best, as a much simpler and more effective one will be detailed in the sequel.

A mixture of nitrate of potash and carbonate of soda was prepared, perfectly free from sulphates. The substance to be analysed was prepared with the most scrupulous attention, and, when mixed with the oxidizing agent, introduced into a combustion-tube and cautiously operated upon in the manner usual for organic analysis. The combustion completed, the whole contents were carefully dissolved in distilled water, pure acetic acid added in excess, the resulting solution precipitated with nitrate of barytes, and the sulphur estimated.

The following were the results:—

- | | | | | |
|-----|------------------|------|-----------------|-------------------------|
| I. | 552.5 milligrms. | gave | 63.0 milligrms. | of sulphate of barytes. |
| II. | 726.0 | . | 82.5 | |

Or,—

- | | | |
|-----|--|----------------------------|
| I. | 11.4 per cent. of sulphate of barytes | = 1.57 p. c. sulphur. |
| II. | 11.3 " " | = 1.56 " |

That sulphur then exists in the compound is decided; the quantity however is remarkable, being twice the amount obtained from albumen by Mulder.

Having now determined the quantity of sulphur, we proceed to examine its influence on the formula proposed by Mulder; and it is evident that the amount of carbon, hydrogen and nitrogen having been decided, whilst that of the oxygen has been merely calculated, it is this element alone which will be affected. Now Mulder's formula is $C^{40}H^{31}N^5O^{12}$; but, in order to derange it even to the amount of a single equivalent of oxygen, we should have 3·6 per cent. of sulphur, that is, double the quantity which it contains, supposing, which is now pretty well decided, that the whole of the sulphur in albumen is retained during the process of forming proteine*; and thus the deductions which have been made for the purpose of explaining physiological phenomena remain uninjured, so far as it regards the influence of sulphur.

It is true that, by multiplying the results of the analysis by ten, a different expression is required; but then it must be remembered that the unavoidable errors of analysis are multiplied also. Mulder

* We are informed by Prof. Schœnbein that Mulder by no means assents to his proteine containing sulphur, but firmly maintains the contrary. We understand that he is now preparing for publication some observations on Laskowski's paper, which we shall immediately place before our readers on their appearance; in the mean time it is but fair towards the justly celebrated Dutch chemist to reserve all opinion on the subject. The fact is of such vast importance, that it requires far more than the incomplete researches of one young chemist, although proceeding from the Giessen Laboratory, to be considered as overthrown.—W. F.

indeed made use of this artifice with reference to albumen and fibrine, to show in what he considered the specific distinction of these bodies consisted, and in what condition sulphur and phosphorus might be supposed to exist in them. The latter hypothesis however is no longer tenable, and it seems, from the recent researches in Liebig's laboratory, that sulphur at least is present in very variable proportions*; so that albumen is either a compound of bodies, one of which contains sulphur as an essential part, or else the sulphur is present as a mere mechanical adjunct.

The following plan for determining the sulphur in organic compounds will be found more simple and convenient than most of the others proposed. Fine quartz sand is treated with hydrochloric acid and well washed; the liquid being tested, to ascertain the absence of sulphates. When dried at a high temperature a mixture is formed of one-third chlorate of potash, perfectly free from sulphates and phosphates, and two-thirds sand. The object of the sand is to prevent the too rapid oxidation of the organic body and the risk of a portion being thrown out of the crucible. The body to be examined is now intimately mixed with the above, introduced into a large platinum crucible, and exposed to a high temperature over a spirit-lamp. The process is completed in a few seconds. The contents of the crucible are now to be treated with boiling distilled water, the insoluble portion separated by filtration, and washed until no traces of sulphuric or phosphoric acid remain; and the sulphates and phosphates, which by this plan may be estimated simultaneously, determined by means of a salt of baryta.

St. John's, Isle of Man,
Sept. 18th, 1846.

On the Influence of Protoxide of Nitrogen upon Vegetation.
By M. VOGEL, Jun.

It is generally admitted that nitrous oxide is not capable of sustaining life, although a candle blown out is relighted, and burns with more brilliancy in this gas than in atmospheric air. The rapid combustion of the candle is owing to the easy decomposition of this gas at a high temperature—a decomposition which cannot be effected by the lungs in respiration; while air, which is but a simple mixture of oxygen and nitrogen, readily parts with its oxygen in the act of respiration. I have made some experiments to ascertain the influence of the protoxide of nitrogen on vegetation. The gas which I employed was obtained by heating perfectly pure nitrate of ammonia. I placed some seeds of cress, scattered over a moistened sponge, in a white glass flask, filled with protoxide of nitrogen. The seeds

* In reference to these researches, of which an abstract was given in our last Number, p. 363, we must request the reader to correct an error, kindly pointed out by our correspondent, occasioned by the falling out of one of the types. Under *Albumen* No. 4, the amount of sulphur appears as —303, it should be 1·303.—Ed. *Chem. Gaz.*

were introduced into the flask under water, and all atmospheric air removed as much as possible from the pores of the sponge by gently pressing it. A sufficient quantity of water was left in the flask to produce germination; the vessel was then closed hermetically.

For the sake of comparison, I placed in a flask filled with air another sponge covered with seeds of cress. In the course of a few days the seeds in the last vessel were developed, and began to form leaves. The case was different with the seeds in the protoxide of nitrogen; there not the least trace of the development of the germ could be observed; nevertheless the seeds had swollen, and were covered with a mucous layer, without having experienced any other change which could lead to the supposition of their having germinated. After two weeks I removed the sponge with the seeds from the flask; but as soon as they were exposed to the air they began immediately to germinate, proving that during their stay in the protoxide of nitrogen they had not lost the power of germinating, while they do not germinate when they have been in contact for some time with several other gases.

The gas in which the seed had been kept for two weeks had experienced no alteration; it did not contain the least trace of carbonic acid, and still set light to the glowing wick of a candle.

To ascertain the influence of this gas on plants already developed, I introduced into a flask filled with protoxide of nitrogen a sponge covered with plants of cress perfectly formed, observing the precautions mentioned above; for two days the young plants continued unaltered, but on the third they acquired a yellow colour, and towards the end of the week they drooped. Exposed to the air, they re-assumed in a few days their verdure and erect position.

It must be remarked, that the above experiments were made not only upon seed, but also upon the plants, and that the oxide of nitrogen was exposed to the direct rays of the sun, and kept in the shade, but that in neither case decomposition of the gas was effected. —*Journ. de Pharm.*, August 1846.

Chemical Examination of Goose-fat and Oleic Acid.

By Dr. J. GOTTLIEB.

[Continued from p. 361.]

Action of Oxygen upon Oleic Acid.—Bromeis observed that oleic acid absorbed very rapidly, at the ordinary temperature, about 20 times its volume of oxygen, without a trace of carbonic acid being formed. The author found by analysis that the oxygen had combined with 1 equiv. hydrogen of the oleic acid to form water, and that moreover 1 atom of oxygen had entered into combination with a residuary body. The quantity of water formed is however too small to be observed, and much less to be proved. But a different result occurs when oleic acid is exposed at a high temperature to the action of oxygen; the oleic acid soon acquires a rancid odour, melts more readily, and at last becomes yellowish; it then no longer

solidifies completely at a low temperature. The analysis of such an acid yielded—

Carbon	73·20	73·27	34 =	2550·0	73·64
Hydrogen	12·11	12·02	33	412·5	11·91
Oxygen	14·69	14·71	5	500·0	14·45

Elaidic Acid.—When pure oleic acid is treated, in the manner described by Meyer, with nitrous acid, it soon congeals to a perfectly white crystalline mass. If precisely the proper quantity of nitrous acid be employed, the melting-point of the solidified elaidic acid is not much below that of the pure elaidic acid. The oleic acid is almost entirely converted into elaidic acid. On analysis it yielded the same composition as Meyer found, only the formula requires to be somewhat altered, owing to the new equivalent for carbon. Its composition is—

	Gottlieb.			Meyer.					
Carbon	76·57	76·52	76·39	76·52	76·57	76·45	36 =	2700	76·69
Hydrogen ...	12·06	12·17	12·30	12·18	12·24	12·33	34	425	12·06
Oxygen	11·37	11·31	11·31	11·30	11·19	11·22	4	400	11·35

The formula of the silver salt is consequently $C^{36}H^{33}O^3$, AgO , and that of the æther $C^{40}H^{38}O^4$. On considering the composition and formula of the elaidic acid and its salts, it is seen that it agrees perfectly with that of oleic acid. Both acids are quite similar in the solidified state, for the elaidic acid exhibits the peculiarity observed in oleic acid, that of expanding on solidification; but while oleic acid crystallizes from cold alcohol in long needles, elaidic acid separates in large laminæ. Oleic acid does not redden blue litmus-paper, while elaidic acid has a strong acid reaction. The difference of the melting-point likewise affords a character for distinguishing these acids. Moreover, neutral elaidates are very easily prepared. Elaidic acid in the fluid state is likewise oxidized in the presence of atmospheric air or oxygen, although this absorption of oxygen proceeds far more slowly than with oleic acid. It is consequently necessary, in those operations in which the elaidic acid has to be warmed above 113° , to prevent the access of the oxygen of the atmosphere by suitable means. The conversion of oleic acid into elaidic acid, without any alteration in composition and atomic weight of the former, is a fact which cannot yet be explained, especially as the quantity of nitrous acid, which suffices to convert very large quantities of oleic into elaidic acid is so small as to render the supposition of a chemical action of the nitrous acid on the oleic acid very improbable. Boudet made a very important observation on this point, that a mixture of 2 vols. nitric oxide and 1 vol. of oxygen are absorbed by olive oil in tolerable quantity without leaving a residue of any gaseous body; the same applies, according to the author, to oleic acid; the oil or the oleic acid gradually become more turbid, and at last solidify to elaidine or elaidic acid. This proves that the nitric acid does not oxidize the carbon of the oleic acid to carbonic oxide or carbonic acid in its metamorphosis, as neither of these two gases

nor nitrogen gas is perceptible above the oleic acid. When oleic acid, which has been made to solidify in a glass tube under dry nitrous acid, is warmed in a suitable apparatus with water, it gives off no gaseous body excepting a small quantity of nitrogen; so that the nitrous acid cannot be considered to be absorbed undecomposed, as it would then yield a far greater quantity of nitric oxide, which the author was never able to observe in numerous experiments varied in every possible manner.

Pelouze and Boudet observed that ammonia was formed in the action of much hyponitric acid upon elaidine, which the author has confirmed by his observations. When crude elaidic acid is dissolved in a little spirit immediately after its production, and then formed into a paste with an excess of hydrate of lime, an ammoniacal alcoholic liquid can be obtained from it by distillation in a bath of chloride of calcium, which contains at the same time an oily body insoluble in water, combining neither with acids nor with bases, and which must be regarded as a further product of the action of nitrous acid upon oleic acid. This body possesses a peculiar odour, which is identical with that of the crude elaidic acid, and the same therefore which communicates the peculiar odour to the so-called *un-quantum oxygenatum*.

The above experiments prove that the conversion of the oleic acid into elaidic acid is accompanied by a contemporaneous chemical change. It remains now to be shown that it is precisely this chemical change which produces the alteration in the physical properties of the oleic acid. The observation of all chemists who have hitherto investigated this subject proves that when the above reaction is allowed to proceed further, no conversion of the oleic acid occurs. The mass remains fluid, but is capable of causing the formation of elaidic acid in fresh portions of oleic acid. When some elaidic acid is heated to melting in a test-tube with moderately dilute nitric acid, which is free from all nitrous acid, no action takes place. If some copper shavings are now thrown into the nitric acid, a lively evolution of nitric oxide is produced, which passes through the stratum of elaidic acid, and is immediately converted above it by the oxygen of the air into nitrous acid, and is absorbed by the elaidic acid. At the same time sufficient heat is developed to keep the elaidic acid fluid. When the elaidic acid has been exposed for about a quarter of an hour to the action of the nitrous acid gas, it is converted into a heavy tenacious fluid body, which appears colourless and sinks in water. Preserved under water, small quantities of colourless gas (probably nitrogen gas) are slowly liberated from it. If this body be freed, by washing with water, from all nitric acid, and then mixed with about 20 times its weight of oleic acid, the mixture gradually solidifies to crude elaidic acid. This process of solidification is sometimes not terminated in 8 or 10 days; it proves however that a chemical change, caused in the mass of oleic acid by the nitrous acid, is the cause of the formation of the elaidic acid, even when all free, otherwise essential, nitrous acid has been excluded.

Action of Oxygen upon Elaidic Acid.—When elaidic acid is exposed for some hours to the atmosphere at a temperature of 212° , it solidifies on cooling it is true, but between the crystals there is a liquid substance, which leaves oil stains on paper on submitting the acid to pressure. To observe the gradual change of the elaidic acid by exposure to the air, it was left for 14 days at a temperature of 149° , when its melting-point slowly descended. At the same time the acid acquired a rancid, very disagreeable odour, which called to mind that of the crude heated oleic acid, and was partly volatilized, as a beaker placed over the vessel containing the acid became coated with oil-drops possessing a very rancid and aromatic odour. After the lapse of the above time, the elaidic acid was converted into a tenacious mass, which had a yellowish colour and smelt like poppy-oil. It could not be reconverted by nitrous acid into elaidic acid, and when spread on a glass plate dried slowly. The analysis of this substance yielded—

Carbon	69.22	36	=	2700.0	69.01
Hydrogen	10.58	33		412.5	10.54
Oxygen	20.20	8		800.0	20.45

It may therefore be regarded as oxidized oleic acid, $C^{36} H^{33} O^5 + 30$.

The assertion of Boudet and Pelouze, that margaric acid dissolved in oleic acid is likewise converted into elaidic acid by nitrous acid, is incorrect according to the author.

Products of the Distillation of Oleic Acid.—When oleic acid or fats containing oleine are submitted to dry distillation, along with the known products considerable quantities of capric and caprylic acids are condensed, and remain dissolved in the liquid hydrocarbons of the distillate. To separate them from the other bodies formed at the same time, it is best to digest what has passed over with a tolerably dilute solution of carbonate of soda, agitating frequently, when the above acids, together with sebacic and some undecomposed oleic, as also some traces of acetic acid, combine with the soda. The dilute saline solution is now quickly evaporated to free it as much as possible from the adherent volatile hydrocarbons. When the solution is tolerably concentrated, and the odour of the hydrocarbons has greatly disappeared, it is decomposed in a retort with tartaric acid, upon which the volatile fat acids are distilled off; they are combined with barytes, and then separated according to the method described by Lerch. Their identity with the capric and caprylic acids of Lerch was proved by analysis*.

When the barytic salts of the two acids have almost entirely separated, but little mother-liquor is left, which still contains the barytes salts of one or two acids. Judging from the odour and the other external properties of the eliminated acids, they were a mixture of valerianic and butyric acids; this however must be confirmed by more accurate experiments. Not a trace of caproate of barytes could be detected.

* See Chem. Gaz., vol. ii. p. 377.

When pure oleic acid is distilled, the quantity of sebacic acid formed is pretty considerable; capric and caprylic acids are at the same time produced; the latter therefore do not owe their origin to the products of oxidation of oleic acid contained in the crude acid. But in proportion as the oleic acid is altered by the air or in the organism, the quantity of sebacic acid diminishes, while that of the capric and caprylic acids remains the same; it is indeed from this cause that Bromeis could obtain no sebacic acid from the oleic acid of butter, which is always contaminated with large quantities of its products of oxidation. But since the oleic acid of butter also contains pure oleic acid, but only in small quantity, it must also yield sebacic acid on distillation, which the author confirmed by experiment. In the distillation of elaidic acid, which, as is well-known, passes over for the greater part undecomposed, the formation of these two acids could not be observed, which is remarkable, considering the great chemical resemblance of oleic acid to elaidic acid. —*Ann. der Chem. und Pharm.*, lvii. p. 33.

On the Red and Yellow Pigments of Safflower.

By A. SCHLIEPER.

One of the most remarkable investigations in organic chemistry that have recently been published is that of M. Preisser on colouring substances*. This chemist arrived at such beautiful and surprising results, that they merely required confirmation to acquire the greatest importance. I have submitted the colouring principles of safflower to examination, and must unfortunately confess, that not only can I not confirm the results of this chemist, but that I have not found one single word of truth in the whole of his investigations.

Safflower, one of the most valuable, beautiful, but at the same time least permanent of colouring principles, contains two pigments, a red and a yellow one; the former only is employed in the arts, and it is on this that the value of the safflower depends, the yellow pigment not being turned to any account. To discover the relations between the two pigments occurring in the plant, perhaps to convert the one into the other, were the principal objects of this investigation, which led to the following results:—

Yellow Pigment of Safflower.—To obtain this pigment, 40 lbs. of good Bengal safflower were extracted with water until the latter was coloured but faintly yellow; the dilute liquids were acidified with acetic acid, and treated with an excess of a solution of acetate of lead; a white flocculent precipitate immediately formed, which was a combination of oxide of lead with the gummy or albuminous constituents, while the combination of the oxide of lead with the yellow pigment remained dissolved in the acetic acid; to obtain the latter, the liquid filtered from the precipitate was neutralized with ammonia, when it fell as a voluminous, flocculent, dirty, orange-coloured pre-

* This paper was given entire in the second volume of this journal, p. 328.—*Ed. Chem. Gaz.*

precipitate. The separation of the colouring substance from the lead compound could only be partially effected by sulphuretted hydrogen; the liquid filtered from the sulphuret of lead was pale yellow, and became darker by the addition of alkalis; most of the pigment however remained with the sulphuret of lead; for when the latter was treated with water rendered alkaline, it coloured it dark brown. The decomposition was best effected by means of dilute sulphuric acid; but as some few preliminary experiments showed that the yellow colouring principle is readily oxidized in the air, all the operations had to be carried on protected as much as possible from the atmosphere. Since a small excess of sulphuric acid could not be avoided in decomposing the lead precipitate, some acetate of baryta was added to the dark yellow liquid filtered from the sulphate of lead, which after filtration was evaporated in a large retort. The syrupy mass was now treated with absolute alcohol, which left a mixture of gum, albumen, &c. in the form of a grayish-yellow coagulated mass; the dark brownish-yellow and clear solution of the colouring substance in alcohol was then also evaporated with exclusion of the air; and when the residue had the consistence of a syrup, mixed with an excess of water, which dissolved the pure pigment with a beautiful yellow colour, but left undissolved the oxidized or altered colouring substance in the form of a brown sediment.

The yellow pigment of the safflower has the greatest resemblance to the so-called extractive substances; its aqueous solution cannot be exposed for any time to the air, still less heated with access of air, without experiencing some change; it soon deposits a brown substance, which is insoluble in water, but very readily soluble in alcohol, and which is oxidized extractive substance. The aqueous solution of the yellow pigment has an acid reaction; it is of a dark brownish-yellow colour, and its tinctorial power is very great; it has a bitter saline taste and a peculiar odour.

As the yellow colouring substance is so readily decomposed, it was not possible to obtain sufficient of it in a pure state for analysis; the only plan was to analyse some compound in which it would be unexposed to the decomposing influences of the atmosphere; for which purpose the lead compound was selected, from its being possible to obtain it perfectly pure; and the colouring substance, when once combined with oxide of lead, no longer oxidizing.

Since the lead compound of the oxidized colouring substance is nearly insoluble in dilute acetic acid, and that of the pure pigment very soluble, the two could be easily separated; some acetic acid was added to an aqueous solution of the colouring substance, and then an excess of neutral acetate of lead, which produced a dirty brown precipitate, a combination of the oxidized colouring substance with oxide of lead; the clear yellow liquid filtered from this was then treated with ammonia, when the lead compound of the pure colouring substance separated in voluminous dark yellow flakes. The well-washed precipitate, dried at 212° , was submitted to analysis.

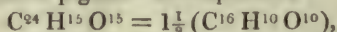
Carbon	..	..	17.85	16 =	200.0	18.40
Hydrogen	..	..	1.92	10	125.0	1.92
Oxygen	..	..	..	10	100.0	15.39
Oxide of lead..	63.61	63.54	..	3	4183.5	64.26

As on igniting it with soda-lime a small amount of nitrogen was detected, one nitrogen analysis was made; 1.4 grm. substance yielded 5.0 cub. centim. moist nitrogen, which is far from forming half a per cent., and may consequently be neglected:—

The formula $3\text{PbO} + \text{C}^{16}\text{H}^{10}\text{O}^{10}$ cannot lay claim to any other value than that of exhibiting, by comparison with the composition of the oxidized colouring substance, the action of oxygen on this class of compounds; for which purpose the brown flocculent precipitate was likewise submitted to analysis: after desiccation at 212° , it yielded—

Carbon	38.42	24 =	1800.0	38.75
Hydrogen	3.21	12	150.0	3.23
Oxygen	28.95	13	1300.0	28.01
Oxide of lead ..	29.42	1	1394.5	30.01

Now if we compare the formulæ of the oxidized and unoxidized colouring substance with one another, leaving entirely out of consideration the amount of oxide of lead, we obtain for the composition of the unoxidized pigment the expression



and for the composition of the oxidized substance the expression $\text{C}^{24}\text{H}^{12}\text{O}^{13}$. It is seen at once that the entire change in this case consists merely of a separation of water, and an oxidation of the hydrogen. De Saussure says that the oxidation of extractive substances is accompanied with an evolution of carbonic acid; but this does not apply in the present instance, for a comparatively small quantity of the solution of the colouring substance was heated in a very large retort filled with air without any carbonic acid being perceptible.

Carthamine, or red Pigment of the Safflower.—This was prepared by the usual process; safflower, freed by washing with water from the yellow pigment, was formed into a paste with water containing 15 per cent. crystallized carbonate of soda, and set aside for some hours. In this interval the whole of the red colouring substance had dissolved in the alkaline liquid, while the safflower had acquired a dirty yellow colour; this latter was pressed and removed, the red liquid nearly neutralized with acetic acid, and then cotton immersed in it, upon which the whole of the carthamine is precipitated, when care is taken to destroy the alkaline reaction of the liquid by the addition of a little acetic acid from time to time. After 24 hours the cotton was removed and washed; the residuary yellowish-red liquid contained no more carthamine. The cotton was now placed in water containing 5 per cent. crystallized carbonate of soda, and left in contact with it for half an hour; by this process an alkaline solution of the pure colouring principle was obtained, as the cotton readily parts with it when placed in contact with alkalis. Since the carthamine

experiences a continued decomposition when in contact with alkalies, it is advisable to shorten those operations in which alkalies must be employed as much as possible. As soon as the colour had been extracted from the cotton, the solution was supersaturated with citric acid, when the previously clear, dark yellowish-red liquid suddenly filled with a light, flocculent, beautiful carmine precipitate of carthamine. I have often tried to precipitate the colouring substance directly from the alkaline liquid by acids, without previously combining it with cotton, but always obtained in this way a very impure product. The precipitate was washed several times by decantation and filtered, which is very easy as long as the liquid contains any salts; but when this is no longer the case, it is almost impossible, for the finely-divided carthamine passes through all the pores of the filter. While moist, it forms a voluminous, very finely-divided mucilaginous precipitate, which on drying shrinks excessively, and can scarcely be removed from the paper. Dried in thin layers upon paper, it coats it with a most brilliant green metallic lustre, by no means inferior to that of murexide and hydroquinone.

As it was impossible to separate the carthamine from the filter, this was torn into small pieces and digested repeatedly with strong spirit, which dissolved the whole of the colouring substance; but a large quantity was requisite. The alcohol was distilled off from the clear dark red solution in the water-bath, and the residuary blackish-red liquid evaporated in a dish over sulphuric acid *in vacuo*. Very soon a thick, brilliant, green, glittering crust of carthamine formed on the surface, which from time to time sunk to the bottom and was renewed. The bottom of the dish became likewise covered with thick crusts of carthamine, which appeared to possess a crystalline structure; however, carthamine, even under a very high magnifying power, always appeared amorphous. The liquid from which it was deposited had a reddish-yellow, highly tinctorial colour, and contained, as I shall presently show, a new body, which is formed by the oxidation of the carthamine. To the whole contents of the dish 3 to 4 times its volume of water was added, by which the newly-formed yellow colouring substance was dissolved, and the carthamine remained, being almost insoluble in water; the latter was now brought on a filter, and washed with water until this acquired a pure red colour. After desiccation the pure carthamine formed a compact granular powder, of a blackish-green colour, acquiring metallic lustre on friction, and only exhibiting the red colour when very finely divided.

For analysis it was dried at 212° , when it yielded—

Carbon	56.90	56.88	56.92	14 =	1050	56.75
Hydrogen	5.61	5.60	5.61	8	100	5.40
Oxygen	37.49	37.52	37.47	7	700	37.85

A small quantity of nitrogen was also found in it, not exceeding 0.3 per cent., which does not form one atom to several hundred atoms of carbon, and may therefore be neglected.

I long endeavoured to determine the atomic weight of carthamine,

but in vain; the only compound which I could select was the lead salt, but in every preparation I obtained compounds of different composition. The only way to prepare this compound was to precipitate an ammoniacal solution of carthamine with neutral acetate of lead, when a more or less dark reddish-brown precipitate is obtained; it all depends whether the solution of lead is a little acid, basic or neutral; for the carthamine has such weak acid properties, that a large excess of it is not even capable of destroying the alkaline reaction of one drop of ammonia or barytic water. Lead salts of four different preparations were analysed; one gave 25 per cent., another 42.59, a third 68 per cent. oxide of lead. To ascertain whether the carthamine possessed a constant composition in these compounds, one was analysed, and gave—

	Found.	Equivalents.	Calculated.
Carbon	56.23	14	56.75
Hydrogen	5.70	8	5.40
Oxygen	38.07	7	37.85

which numbers agree therefore accurately with the composition of carthamine.

Before proceeding to describe the properties of carthamine, I will briefly notice the experiments of M. Preisser. This chemist, in preparing carthamine, likewise exhausts the safflower with water to remove the yellow colouring principle, and then treats it with water rendered alkaline by soda, in order to extract the red principle. "The alkaline liquid is subsequently precipitated by hydrate of lead, which forms an insoluble lake of carthamate of lead. This salt, well-washed, is decomposed by an excess of sulphuretted hydrogen. It is filtered, and a light yellow-coloured liquid is thus obtained, which yields white acicular crystals by spontaneous evaporation, or immediately if sufficiently concentrated, and which constitute pure carthamine*."

To test this process of M. Preisser, I followed his description accurately. In the first place I prepared his so-called hydrated oxide of lead, by precipitating a solution of nitrate of lead with ammonia; but which, according to Arppe, is nothing more than basic nitrate of lead, $2(3\text{PbO}, \text{NO}^3) + 3\text{HO}$, and then added the well-washed salt to the alkaline solution of the carthamine. The oxide of lead however remained as white as before, and only after standing 24 hours had it acquired a faint yellowish-red colour, while the supernatant alkaline liquid still contained the whole of the carthamine which could be precipitated from it by the addition of acids. As it was not possible to obtain in this manner a combination of carthamine with oxide of lead, I followed the method above described of precipitating an ammoniacal solution with acetate of lead; the carthamate of lead so obtained was mixed with a little water and decomposed with sulphuretted hydrogen; the yellowish liquid filtered from the sulphuret of lead contains not a trace of carthamine, as not the slightest change could be produced in it by any reagent,

* Chem. Gaz., vol. ii. p. 351.

and on evaporation it left scarcely any residue; while Preisser states of his crystallized carthamine, that it is instantly converted into the red modification, or carthamine, by contact with alkalis and air. The whole of the separated carthamene is, on the contrary, mixed with the sulphuret of lead, and may easily be extracted from it, with all its properties, by alkalis and alcohol.

We now see upon what the statements of M. Preisser, respecting the decolorization of the colouring principles, are founded.

Carthamine is a dark brownish-red powder, with a greenish iridescence, and exhibits in thin layers, or in an alcoholic solution, the most beautiful purple colour. It is very sparingly soluble in water, and merely colours it faintly red; it is far more soluble in alcohol, especially at a gentle heat; when a drop of the solution is evaporated on a watch-glass, it becomes coated with a metallic green iridescent pellicle. Both the alcoholic as well as the aqueous solutions are soon altered by boiling, acquiring a yellowish colour, which remains on cooling. Carthamine is perfectly insoluble in æther; it is dissolved in every proportion by carbonated or caustic alkalis; however, it cannot be considered to possess the properties of an acid, as it is quite impossible to destroy the alkaline reaction of a drop of solution of soda by it: it must be enumerated among the perfectly neutral substances. Few bodies are so unstable as carthamine in its solutions. The alkaline solutions are constantly undergoing rapid decomposition, no matter whether the access of air be prevented or not; in the first case however the decomposition proceeds more slowly. A solution of a little carthamine in very dilute caustic potash absorbed half its volume of oxygen.

The combination of carthamine with soda, which Döbereiner described as crystallizing in colourless silky needles, I could not obtain, and have every reason to believe that it does not exist. Carthamine is dissolved by carbonate and caustic soda, and also by ammonia, with a deep yellowish-red colour, and may be precipitated from these solutions by the addition of an acid. The ammoniacal solution yields with corrosive sublimate a red precipitate, which disappears on the addition of an acid; no precipitate is caused by a solution of chloride of calcium or chloride of barium. Barytic water dissolves carthamine, forming a yellowish liquid, which is decomposed on standing, but from which the carthamine immediately after solution may be precipitated by acids. Perchloride of iron produces in the ammoniacal solution a brownish-red precipitate, probably a mixture of peroxide of iron with carthamine; protochloride of tin yields a yellowish-brown precipitate soluble in acetic acid, and which also dissolves in the mother-ley on the application of heat, the carthamine undergoing change. Bichromate of potash precipitates the carthamine from an ammoniacal solution, but on heating, the whole dissolves with oxidation of the latter to a yellow liquid. Carthamine dissolves with a red colour in concentrated sulphuric acid, from which water does not separate it. It is at first precipitated from an alkaline solution by nitric acid, but very soon changes; the flakes become brown, and dissolve when heated to a yellow liquid, which

yields yellow combinations with oxide of lead. It is moreover precipitated from its solutions by sulphurous acid, but on being heated with it dissolves to a yellow liquid.

Carthamine experiences no alteration by sulphuret of ammonium. Salts of oxide of copper produce a peculiar decomposition in an ammoniacal solution of carthamine; on adding to the latter a solution of ammonio-sulphate of copper, a dark brown, almost black precipitate is obtained, while the filtered liquid has a green colour. The precipitate is insoluble in muriatic acid; treated with a solution of caustic potash and ammonia, it forms brown flakes and a yellow solution. According to all experiments, this compound contains protoxide of copper in combination with a yellow pigment, which is formed by the oxidation of the carthamine at the expense of the oxygen of the oxide of copper. As the compound could not be obtained free from ammonia, it was useless to analyse it. The moist black precipitate was decomposed after the addition of a little acetic acid by sulphuretted hydrogen, and the sulphuret of copper removed by filtration; the filtered brownish yellow liquid was precipitated, after the addition of ammonia, by sugar of lead in yellow flakes, the quantity of which however was not sufficient for analysis.

I have also submitted the yellow body previously mentioned to close examination; the aqueous liquid containing it was concentrated by evaporation, and set aside for some weeks, in which time a small quantity more carthamine had subsided, which was separated by water. The liquid freed from this was evaporated to dryness in the water-bath, and again dissolved in water, when but a very small insoluble residue was left. Even on repeating this process several times, to ascertain whether the body were altered by heating the solutions exposed to the air, but a very inconsiderable residue was left on solution in water, showing that it differs essentially from the yellow pigment contained originally in the safflower. It dries on evaporation in the water-bath to a dark brown gummy mass, which becomes moist in the air, and is consequently not suited for analysis. For this purpose therefore the lead compound was selected, which however, like the combination of carthamine with lead, yielded a varying amount of lead in different preparations; nevertheless it was easy to calculate, after deducting the amount of oxide of lead, the composition of the body in combination with it.

To the yellow solution of the substance some acetic acid, and then a solution of acetate of lead, were added, upon which the scanty dark-coloured precipitate which formed in the acid liquid was filtered and thrown aside; the deep-yellow filtered liquid was now treated with ammonia, when a beautiful bright orange precipitate formed, which, after washing and drying at 212° , was submitted to analysis. It yielded 60.25–59.99 per cent. oxide of lead, deducting which we obtained for the carbon, hydrogen and oxygen in 100 parts the following numbers:—

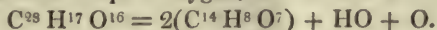
Carbon		51.40	51.08	14 =	1050.0	51.53
Hydrogen		4.59	4.08	7	87.5	4.29
Oxygen		44.84	44.18	9	900.0	44.18

The carthamine lost therefore by boiling with alcohol 3 atoms oxygen and 1 water.

I have already stated that carthamine is likewise readily decomposed by alkalies. To ascertain more precisely the nature of this process, a solution of carthamine-ammonia was set aside until wholly decomposed. Upon slightly supersaturating the yellow liquid with acetic acid, a beautiful coffee-brown coloured substance separated in flakes, which dissolved in alkalies, and were again precipitated by acids. The quantity sufficed merely for one combustion; it yielded—

Carbon.....	52.95	28 =	2100.0	53.67
Hydrogen	5.60	17	212.5	5.44
Oxygen	41.45	16	1600.0	40.89

In this body (A) we have 2 equivs. carthamine combined with 1 equiv. water and 1 equiv. oxygen,



It forms therefore the intermediate state between carthamine and that substance which is contained in the liquid filtered from the body A.

The filtered yellow liquid, which contained free acetic acid, was treated with a solution of acetate of lead, and the precipitate which formed collected on a filter; unfortunately however I obtained too little of this compound for analysis. The yellow liquid deposited, on the addition of ammonia, another salt of lead in large yellow flakes, which after washing and drying was submitted to analysis, and gave 70.34–69.43 oxide of lead, deducting which we obtained for the organic substance the following numbers:—

Carbon.....	49.20	14 =	1050.0	49.12
Hydrogen	4.02	7	87.5	4.09
Oxygen	46.78	10	1000.0	46.79

This substance therefore is the highest state of oxidation of carthamine, or carthamine + 4 equivs. oxygen — 1 equiv. water; and the action of alkalies upon carthamine is a purely oxidizing one. All attempts to convert the once-oxidized and modified carthamine back again into the original carthamine proved fruitless.—Liebig's *Annalen*, lviii. p. 357.

On the Presence of Copper in the Bile.

By E. F. GORUP-BESANEZ.

As long ago as 1838 Duvergie found copper in the human organism, and this result has been partly confirmed and partly denied by several chemists. It has moreover formed a subject of dispute between Danger and Flandin and Duvergie, which, at least partly, depends upon misunderstanding. Quite recently Bertozzi's result has been again taken up, who detected copper in biliary calculi. Heller and the author have confirmed his statement. Braunsen not only found copper in several biliary calculi, but also in healthy

human bile. The author also obtained the latter result. He incinerated about 2 grms. of dark brown, friable, human gall-stones with the addition of nitric acid, and found that the ash fused to a pale blue mass, which, after having been dissolved in dilute muriatic acid and filtered, yielded a brown precipitate with sulphuretted hydrogen, and a dark blue precipitate with ferrocyanide of potassium. An iron wire, on immersion in the slightly acid solution, soon became covered with a metallic film of copper. Hence copper and iron existed in the ash of the calculi. 60 grs. of mucus from the gall-bladder, with the biliary colouring matter (of about 12-15 bladders) as it occurs after precipitation from the bile by alcohol, were completely incinerated with the aid of nitric acid. The slightly pale blue ash was dissolved in dilute sulphuric acid, filtered, part of the acid volatilized by heat, and a current of sulphuretted hydrogen passed through the acid solution. The first bubbles of gas immediately produced a dark brown colour, and a tolerably copious brown precipitate gradually formed. This was collected on a small filter, washed, dried, and heated with nitric acid, whereupon sulphur separated, and the liquid assumed a bluish-green colour. When this was neutralized, it gave a brown precipitate with sulphuretted hydrogen, a brownish-red precipitate with ferrocyanide of potassium, and an azure-blue colour with ammonia. The solution, after having been acidified with muriatic acid, covered a platinum wire, which was united to a piece of zinc forming a galvanic circle, in a few minutes with a reddish deposit of metallic copper. The author recommends the use of platinum and zinc for detecting very small quantities of copper, instead of iron, which is ordinarily used, as the latter is acted upon by the free acid, and hence the reaction is sometimes not sufficiently distinct. Moreover, in another experiment, in which a bright iron wire was placed in the solution of the ash of human bile in sulphuric acid, the reaction of copper appeared, as also in a third, in which the solution of the ash was treated with sulphuretted hydrogen. An experiment made upon ox-gall likewise indicated the presence of traces of metal precipitable by sulphuretted hydrogen; but the quantity of the precipitate was too small for determining whether the reaction arose from copper or lead. In subsequently repeating this experiment with the ash of 4 ox-galls, the platinum in the galvanic circle was covered with a gray deposit, which induces the belief of the presence of lead. From the above experiments it is evident that the views of Bertozzi, who never found copper in the bile, but did in gall-stones, and hence concluded that copper might give rise to biliary concretions, are unfounded. There can be no doubt as to the source of the copper in the bile, as it exists not only in a great many cooking utensils, but also in many plants.—*Buch. Rep.*, xlii.

On the Fairy Rings of Pastures. By Prof. J. T. WAY.

After describing these patches, with which most persons are familiar, the author states that the grass of which such rings

are formed is always the first to vegetate in the spring, and keeps the lead of the ordinary grass of the pastures till the period of cutting. If the grass of these fairy rings be examined in the spring and early summer, it will be found to conceal a number of agarics, or "toad-stools," of various sizes. They are found situated either entirely on the outside of the ring, or on the outer border of the grass which composes it. Decandolle's theory, that these rings increased by the excretions of these fungi being favourable for the growth of grass, but injurious to their own subsequent development on the same spot, is shown to be insufficient to explain the phenomena. A chemical examination of some fungi (the true St. George's Agaric of Clusius, *Agaricus graveolens*) which grew in the fairy rings on the pasture around the college at Cirencester, was made. They contained 87·46 per cent. of water, and 12·54 per cent. of dry matter. The ashes of these were found to contain—

Silica	1·09
Lime	1·35
Magnesia.....	2·20
Peroxide of iron.....	trace.
Sulphuric acid	1·93
Carbonic acid	3·80
Phosphoric acid	29·49
Potash.....	55·10
Soda	3·32
Chloride of sodium.....	0·41
	98·69

The abundance of phosphoric acid and potash, existing no doubt as the tribasic phosphate of potash ($3\text{KO}, \text{PO}_5$), which is found in these ashes, is most remarkable.

The author's view of the formation of these rings is as follows:— A fungus is developed on a single spot of ground, sheds its sporules, and dies; on the spot where it grew it leaves a valuable manuring of phosphoric acid and alkalies, some magnesia and a little sulphate of lime. Another fungus might undoubtedly grow on the same spot again; but upon the death of the first the ground becomes occupied by a vigorous crop of grass rising like a phoenix on the ashes of its predecessor. It would thus appear that the increase of these fairy rings is due to the large quantity of phosphated alkali, magnesia, &c. secreted by these fungi; and, whilst they are extending themselves in search of the additional food which they require, they leave on decaying a most abundant crop of nutriment for the grass.—*Athenæum*.

Chemical Examination of some kinds of Marl.

By DR. KROCKER.

As is well known, marl is used to improve both the physical as well as the chemical condition of the soil; but, as apparent from the ordinary names of chalk-marl, clay-marl and sandy-marl, it varies

considerably in its composition, and must consequently exert a different influence on the soil. So, for instance, a clay-marl is best suited for a sandy soil, while it would rather prove injurious to a heavy soil; chalk-marl would most improve a soil which contained little calcareous matter, &c. But as the marl contains, besides these constituents, also alkaline salts, attention must likewise be paid to these in the choice of a marl. Just as in liming a clay-soil, soluble alkali is conveyed to the plants by the decomposition of the aluminous silicate, the same effect will also be obtained, especially with an alkaline marl. It was found that with different amounts of carbonate of lime and alumina, the more calcareous the marl under otherwise like conditions, the more alkali did it contain in a decomposed soluble state; while the amount of water in the air-dried marls increased with the amount of alumina. All the marls examined, on being heated with hydrate of lime, gave off ammonia, which was determined according to the method of Will and Varrentrapp, and deserves attention, as undoubtedly the vegetation is advanced by the ammonia added to the soil at the same time with the necessary mineral substances. In the analysis, two portions of marl, each of about 10 grms., were extracted with hot acetic acid, and washed until nothing further was removed, the residue dried at 212° and weighed. The acetic solution was employed to determine the lime and magnesia, the solution of the second portion evaporated after removing the lime by ammonia and carbonate of ammonia, then heated to redness, and the residue extracted with water, when the magnesia remained undissolved, and the potash was determined by chloride of platinum. Only traces of soda, manganese and phosphoric acid could be detected. The amount of water was determined by drying at 212° and subsequent ignition. 100 parts of different kinds of marl examined according to this method yielded—

Carbonate of lime ...	12·275	14·111	18·808	20·246	25·176	32·143	36·066
Carb. magnesia	0·975	trace.	1·228	3·211	2·223	1·544	1·106
Potash	0·087	0·082	0·092	0·091	0·105	0·101	0·163
Water.....	2·036	2·146	2·111	1·311	1·934	1·520	1·555
Alumina, sand and peroxide of iron }	84·525	82·830	76·827	74·325	69·570	64·214	60·065
Ammonia	0 0047	0·0077	0·0988	0·0768	0·0736	0·0955	0·0579

Ann. der Chem. und Pharm., lvii. p. 373.

On Crystallized Oxide of Tin. By J. TÖRMER.

A porous mass of metal was found, after the casting of a bell, at an injured portion of the furnace, in which numerous groups of acicular crystals with very strong lustre occurred. They appeared under the lens to be quadratic prisms with a four-sided summit. The purest crystals were colourless and perfectly transparent, while others had a reddish-gray appearance, and exhibited black particles in their mass; nitric and hydrochloric acid had no action on them; borax and microcosmic salt slowly dissolve them, forming clear pearls. The crystals are quickly reduced with soda upon charcoal to a white

metallic grain, which is converted by nitric acid into a white powder. The crystals undoubtedly consisted of oxide of tin and the interspersed particles of metallic copper.—*Journ. für Prakt. Chem.*, xxxvii. p. 380.

CHEMICAL PREPARATIONS.

On an easy and advantageous Method of preparing Mannite.

By GIOVANNI RUSPINI.

THE author, after passing in review the investigations of those authors who have studied this product, and directing attention to the discovery made by Prince L. Buonaparte, that the aqueous solution of mannite yields by cooling larger and more regular crystals than those obtained from an alcoholic solution, recommends the following method of preparing mannite as highly advantageous in a pecuniary point of view.

Prince L. Buonaparte recommends treating flake manna with boiling alcohol, and after having allowed the mannite to crystallize, removing the whole of the alcohol by filtration and pressure, and then redissolving the cake of mannite so obtained in boiling water. On cooling, superb white crystals are obtained.

M. Ruspini attributes the high price of mannite to three causes,—1st, the loss of a portion of the alcohol employed; 2nd, to the small quantity of product obtained; 3rd, to the use of flake manna (*can-nullata*), the price of which is always high. These inconveniences are avoided by adopting the following method:—6 lbs. of Geracy manna are dissolved over the fire in about half its weight of rain-water in which the white of an egg has been previously beaten; it is then boiled for a few minutes and strained through a woollen bag. The liquid thus obtained solidifies on cooling. It then presents the following characters:—Colour of the mass pale brown, which by trituration forms a liquid resembling common honey. After this operation M. Ruspini separates the mannite by two different processes.

First Process.—After having pressed it strongly in a linen bag, the author dries the granulated and nearly white mannite remaining in the bag (the filtered portion, on the contrary, is highly coloured), then reduces it to a powder, which is dissolved in alcohol of 0.912; and when the solution boils, some animal charcoal is added to it, and it is immediately filtered through paper into a porcelain dish, where the mannite crystallizes on cooling. He thus obtained 30 oz. of crystals as white as snow, and with a mother-of-pearl lustre.

The alcohol separated by filtration, and that obtained by slightly pressing the crystals, may be set aside for another operation, or distilled, and the mannite which it still contained in solution thus separated; but as the latter is always coloured, it must be redissolved and again decolorized.

M. Ruspini has found by experiment that the mannite is not more purgative than manna, and differs in opinion on this point with Prince L. Buonaparte and M. Soubeiran, who assert that the mannite is the purgative constituent of manna; while Berzelius and other chemists have found that mannite does not in the least contribute to render the manna purgative. M. Ruspini is equally opposed to this last opinion.

The *Second Process* differs from the first in this, that instead of drying the cake of amorphous mannite, in order to treat it subsequently with alcohol, nearly an equal weight of cold water is added to it, and it is again pressed; in this manner a product is obtained which is considerably less coloured than before this treatment. The separated coloured liquid may be added to that of the first operation. Lastly, instead of dissolving this white amorphous mannite in alcohol, it is dissolved in a suitable quantity of boiling water to which animal charcoal has been added; the boiling liquid is filtered into a porcelain dish, which is heated in order to evaporate the solution until a pellicle forms, when it is set aside to crystallize. The crystals thus obtained are much larger than those deposited from an alcoholic solution; they are truncated four-sided prisms, perfectly white and transparent.

M. Dalpiaz states that he has repeated the experiments of M. Ruspini, and obtained all the results which he describes.—*Journ. de Pharm.*, August 1846.

Notice respecting the Preparation of the Ferrocyanide of Zinc.

By JONAS.

The author added dilute hydrochloric acid to some pure Paris blue contained in a beaker along with some metallic zinc, in order to decompose by means of zinc the ferrocyanide into iron and cyanide of zinc. Evolution of hydrogen gas took place, which was furthered by gently heating and agitating, and decomposition commenced, when the blue colour of the compound disappeared to make way for a white and turbid one. If the zinc contain lead, as usual, it is eliminated during the operation, and may be removed by decanting the liquid, while any iron contained in the zinc or the muriatic acid remains dissolved in the liquid. The edulcorated precipitate was ferrocyanide of zinc, a white powder insoluble in muriatic acid, but still combined with a little ferrocyanic acid, from which it was freed by again treating it with muriatic acid and zinc, or by dissolving it in caustic potash and precipitating with muriatic acid. In the above reaction the hydrogen in *statu nascenti* enters into combination with the cyanide of iron, which decomposes the chloride of zinc formed into hydrochloric acid and ferrocyanide of zinc, so that the hydrochloric acid is again able to act on the metallic zinc, and keep the process of decomposition going. The compound could not be obtained by merely bringing together cyanide of iron and chloride of zinc.—*Journ. für Prakt. Chem.*, xxxviii. p. 252.

THE CHEMICAL GAZETTE.

No. XCVI.—October 15, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Sulphur on Potash and Soda and their Carbonates.
By MM. FORDOS and GELIS.

It is well known that the products of the action of sulphur on potash and soda, in daily use in medical practice, are designated by the names *hepar sulphuris*, or liver of sulphur. Two of different composition are admitted,—the *hepar* by the dry method, prepared with the alkaline carbonates, considered as a mixture of polysulphuret and sulphate; and that by the moist way, obtained by means of the caustic alkalis dissolved in water, and in which it is said the sulphate is replaced by a hyposulphite of a peculiar composition.

This supposed difference in the state of oxidation of the sulphur in these two compounds, a difference which, as we shall see presently, does not exist, but which is generally admitted, caused Gay-Lussac to compare sulphur to chlorine, which gives with alkalis, chlorides, chlorites or chlorates, according to the relative solubility of the compounds capable of being formed by the different elements engaged.

We have endeavoured chiefly in this memoir to ascertain what becomes of the oxygen previously combined with the alkali. As to the sulphurets formed during the processes, we have nothing to add to the facts already described.

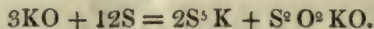
I. *Hepar by the Dry Process.*—We endeavoured first to ascertain the temperature at which sulphur expels the carbonic acid from its combination with potash and soda; and we found that very different degrees of temperature are necessary for the action of sulphur on these two carbonates. With the carbonate of potash the action commenced at 226° F., the melting-point of the sulphur, and could be completed at a temperature of 356° F. The carbonate of soda, on the contrary, required the temperature of 527° F.

The examination of the potash *hepar* has convinced us that sulphuret of potassium and hyposulphite of potash only were formed without the least trace of sulphate, and we were enabled to separate these two products by means of alcohol, which dissolves only the sulphuret.

A normal test-solution of sulphate of zinc was employed to ascer-

Chem. Gaz. 1846.

tain the amount of sulphuret, and the quantity of hyposulphite was determined by a test-solution of iodine. The following formula expresses the reaction of the process:—



By employing less sulphur, a polysulphuret with less sulphur is obtained; but whatever proportions are employed, hyposulphite only is formed, and never sulphate. The hepar of the Codex, and all commercial preparations which we analysed, had a similar composition.

As a red heat is not necessary to the formation of this compound, it appeared natural to suppose that Berzelius and Vauquelin had examined a product which had suffered an alteration by the action of the high temperature to which it had been exposed, and that the sulphate of potash found in it by these chemists, instead of being one of the elements of the reaction, was produced by the decomposition of the hyposulphite. This opinion has been confirmed by the examination we have made into the action of heat upon the hyposulphites of potash and soda, which at a temperature of 572° are transformed into 3 equivs. of sulphate and 1 of sulphuret.

If, instead of the carbonate of potash, carbonate of soda is employed, the same reaction is obtained; but, as we have before mentioned, a much higher temperature is required, a temperature approaching 536° . Thus it is difficult, unless many precautions be taken, to obtain the hepar perfectly free from sulphate, for the hepar is only formed at a temperature approaching that at which the hyposulphite is decomposed. The carbonates of baryta and of lime, which are not attacked by the sulphur but at a very high temperature, far exceeding those capable of being estimated by a mercurial thermometer, furnish a product containing no hyposulphite.

II. Hepar Sulphuris by the Moist Method.—For all that we know of this preparation we are indebted to Gay-Lussac and Berzelius, the latter of whom admits the existence of a hyposulphite of peculiar composition in this compound, in which each equivalent of base would be combined with a quantity of acid containing 3 equivs. of sulphur.

This composition, which appeared singular to Berzelius himself, but which the constancy of his analytical results induced him to admit, is no longer admissible now that the combining proportions of hyposulphurous acid are better known. The probability is that this acid forms neither acid nor basic salts; at least all our efforts to form such combinations have been without success, and we have shown elsewhere that the so-called bibasic hyposulphites SO , MO , supposed to be formed during the action of sulphurous acid on certain metals, have no existence.

We thought that the reaction should be the same as in the preparation of the hepar by the dry method; but it was necessary however to prove this by experiment, for the compound formed during the moist process might possibly be one of the acids of sulphur recently discovered, and the relation of 1 to 3 between the base and

the sulphur indicated by Berzelius, might induce us to believe in the existence of the salt of M. Langlois.

Such however is not the case; the product is always the same whether it be prepared with the caustic or carbonated alkalies, by the moist or by the dry method. Among all the compounds of oxygen and sulphur, hyposulphurous acid is the only one formed, and it exists in the *Hepar sulphuris* in the state of neutral salt, that is to say, that each equivalent of the base saturates a quantity of acid containing 2 equivs. of sulphur. The substance examined was always prepared out of the contact of air; the flask in which the operation was conducted was closed by a bent tube, 0^m.74 long, plunged into mercury. This arrangement of the apparatus allowed us to collect the gases, in case any might be evolved, and we were not a little surprised to find a disengagement of sulphuretted hydrogen during the whole time the sulphur was boiling in the alkaline solution.

This disengagement was accompanied with the production of hyposulphite, varying in each operation, and which was the greater the longer the ebullition was continued. This increase of the hyposulphite prevented us from confirming by means of analysis the atomic relations which we had conceived from theory. It is thus evident that the sulphuret saturated with sulphur decomposes water; and this fact, unknown to chemists, may have frequently led to erroneous results. How is this decomposition of water effected? To give a satisfactory answer to this question, it is necessary to examine the condition of the sulphurets in a state of solution. Henry Rose, in his researches on the sulphurets*, remarked that, on treating the sulphuret of barium by successive small portions of water, in the first portions a solution of hydrosulphate of the sulphuret was obtained, and in the latter oxide of barium; he also remarked that, on concentrating a solution of sulphuret of barium, there was a disengagement of sulphuretted hydrogen, and at the same time oxide of barium was precipitated. Analogous results were obtained from the sulphurets of strontium and calcium; he was led to believe that the sulphurets of the metals of the alkaline earths are transformed into oxides and hydrosulphates of sulphurets at the moment of their solution. This theory, based on experiment, has been adopted by chemists. Can it be applied to the solution of the sulphurets of sodium and potassium? Rose was unable to arrive at a conclusion founded on experiment. Chemists would not readily have admitted the theory of Rose if applied to the solution of the alkaline sulphurets; it is nevertheless the only one which easily explains the reaction of sulphur on the sulphurets, with which we are at present engaged. Suppose that sulphuret of sodium is transformed into oxide and hydrosulphate of sulphuret on solution in water, what takes place on boiling the solution? Alone it undergoes no apparent change, the hydrosulphate of soda not being decomposed at the temperature of boiling water, and the soda and hydrosulphuric acid being in the right proportion for saturation; but if sulphur is added

* See Chem. Gaz., vol. i. p. 118.

the reaction will be different; the sulphur will react on the soda in such a manner as to produce a fresh proportion of sulphuret and of hyposulphite; it will react equally on the hydrosulphate of the sulphuret, and M. Thenard has shown that this reaction gives rise to the production of sulphuretted hydrogen.

It only remains to explain why the results of Berzelius differ from ours. For this it is necessary to relate succinctly the method used by this celebrated chemist. Berzelius did not isolate the compound $S^3 O_3$, MO ; after having prepared, as we did, a solution of *Hepar sulphuris* out of the contact of air, he digested it with the hydrated oxide of copper, in order to deprive it of the sulphur which it contained in the state of sulphuret; then having filtered it he made two determinations,—one of the sulphur of the hyposulphite, and another of the whole of the potash used in the process, and which remained in the solution; he found for 3 equivs. of sulphur 4 equivs. of potash. As he had assured himself, by a previous experiment, that the solution contained hyposulphurous acid, he was induced to believe in the existence of a peculiar hyposulphite, as for 1 equiv. of potash which remained he found 3 equivs. of sulphur in the hyposulphite.

This conclusion would have been rigorously correct if the method of analysis employed by Berzelius had not led him into error, and if some unexpected influence had not caused the oxidation of the sulphur; it is not so, however, and he might have found in his determination even a greater proportion of sulphur, for that which he obtained not only represents the sulphur of the hyposulphite essential to the reaction, but also that of the hyposulphite arising from the decomposition of the water, the quantity of which varies according to the duration of the ebullition; and moreover the sulphur resulting from a third quantity of hyposulphite, which would be formed during the digestion of the sulphuret with the hydrated oxide of copper; for in this case the oxide of copper does not merely exchange its oxygen for an equivalent proportion of sulphur, but it exercises an oxidating effect on the sulphur, as we have repeatedly assured ourselves; and it was the fear of this oxidation, which we foresaw, that caused us to select at the commencement of our experiments the salts of zinc to determine the sulphur.

This property of oxidizing the alkaline sulphurets does not belong only to the blue hydrated oxide of copper; it is also possessed by the calcined oxide of copper employed in organic analysis. The action is exercised equally on the monosulphurets and the polysulphurets, both when hot or in the cold, the quantity of hyposulphite formed varying according to the conditions of the experiment.—*Comptes Rendus*, July 27, 1846.

On the Development of Mineral Substances in the Bones of Pigs.
By M. BOUSSINGAULT.

Bones of a Pig just Born.—The animal weighed, immediately after its birth, 650 grms.; its skeleton, dried in the air, 48.23 grms;

the ashes of the skeleton, 20·73 grms. The perfectly white ash contained—

Phosphate of lime.....	84·1
Basic phosphate of magnesia	11·0
Carbonate of lime.....	4·5
Alkaline salts.....	0·4

Bones of a Pig eight Months old, weighing 60550 grms.—The animal was fed on the usual food, and its skeleton, dried in the air, weighed 2901 grms. The bones of the head contained 47·4 per cent. ash; the ribs, 43·3; the vertebral column, 36·6; the tibia, &c., 49·8 per cent. The bones of the head weighed 653 grms.; the ribs, 276; the vertebræ, 455; the bones of the extremities, 1517 grms. The ash contained—

Phosphate of lime.....	91·3
Basic phosphate of magnesia	3·6
Carbonate of lime.....	3·6
Alkaline salts	1·5

Bones of a Pig 11½ Months old.—The animal weighed, at the same age as the preceding, 60 kilogrms.; 93 days later, during which it consumed 544 kilogrms. potatoes, it weighed 67240 grms.; the skeleton, dried in the air, weighed 3407 grms., and gave 1586 grms. ash, which contained—

Phosphate of lime.....	92·4
Basic phosphate of magnesia	3·8
Carbonate of lime.....	3·4
Alkaline salts	0·4

If we now ask how much the skeleton of each animal increased on an average daily during that period, we obtain for the pig 8 months old, 11·7 grms. for the dried skeleton, 5·5 for the ash, 2·4 for the phosphoric acid, and 2·8 grms. for the lime. The other pig increased, during the 93 days which it lived longer, daily about 6 grms. for the dry skeleton, 2·6 ash, 1·4 phosphoric acid, and 1·6 gm. lime. During the first period, the food contained a great quantity of phosphoric acid and lime, which was not the case subsequently when the food consisted only of potatoes, which yield but 0·01 per cent. ash, consisting of—

Phosphoric acid.....	11·3
Lime	1·8
Magnesia	5·4
Sulphuric acid, potash, soda.....	81·5

In 544 kilogrms. of potatoes, which the pig consumed in 93 days, there were 5440 grms. mineral substances, containing 615 grms. phosphoric acid and 98 lime, while during that time it had absorbed 129 grms. phosphoric acid and 150 lime. There were therefore 52 grms. lime more absorbed than were contained in the ash of the potatoes, a difference which becomes still more considerable when the amount of lime contained in the excretions is taken into consideration; these weighed during the 93 days, after drying, 16·6

grms., and contained 0·013 per cent. lime, so that the lime secreted with them amounted in the whole to 216 grms. The quantity of the assimilated and excreted lime amounts to 268; that taken up with the potatoes, to 98 grms. The water with which the potatoes were prepared contained in 100,000 parts—

Carbonate of lime.....	35·3 = 19·9 lime.
Carbonate of magnesia.....	3·7
Sulphate of magnesia	11·8
Sulphate of soda	20·2
Chloride of sodium	6·9
Silica.....	2·0
Phosphate of lime and iron	traces.
Organic substances, &c.	undetermined.

Now in 93 days the pig had received 900 litres of water, containing, according to the preceding analysis, 179 grms. lime, which added to the 98 grammes contained in the potatoes = 277 grms. lime; consequently more lime than was assimilated and excreted. The water yielded therefore a nutritive substance, which did not exist in sufficient quantity for the nutrition of the pig in the potatoes; and it is probable that if the water had not been so calcareous the pig could not have been kept so long on potatoes only.—*Ann. de Chim. et de Phys.*, xvi. p. 486.

On the Non-existence of Nitrogen in Picrotoxine, with Observations on the Analysis of Nitrogenous Bodies in general. By Profs. ERDMANN and MARCHAND.

Oppermann, Pelletier and Boullay, and Regnault, examined picrotoxine without detecting nitrogen in it; Francis, on the contrary, obtained in two experiments a small quantity of this element. In other respects the results agree, except that Oppermann obtained more than 1 per cent. of carbon too much.

	Oppermann.	Pelletier and Boullay.	Regnault.	Francis.
Carbon	61·5	60·9	60·3	60·26
Hydrogen	6·2	6·0	5·7	5·70
Oxygen	32·3	33·1	34·0	32·74
Nitrogen.....	..	..	..	1·30-0·75

The authors subjected picrotoxine to a very careful examination as to the existence of nitrogen, in order to test the accuracy of the method of determining nitrogen they have followed for some time. They first tried the qualitative method recommended by Lassaigne. Strongly-ignited elder-tree charcoal, obtained from wood that had been exhausted, was ignited with potassium, the mass treated with water and muriatic acid, filtered, and treated with proto-persulphate of iron. No blue precipitate resulted, but the liquid acquired a bluish colour, and had deposited by the next day a fine blue powder. Now since the extremely minute quantity of nitrogen in the charcoal could be detected in this way, some picrotoxine was treated in

the same manner; but not the least indication of nitrogen was perceptible even when considerable quantities were employed. It is therefore possible that Francis did not analyse a perfectly pure body, or that the method followed by him was the cause of the error*.

Eight years ago the authors described a method for the quantitative determination of nitrogen, which agrees essentially with that of Dumas, but to which it has been objected that it is not so accurate as that of Will and Varrentrapp; the authors however show, by a tabular arrangement of numerous results obtained by them and other chemists, that this objection is not well-founded, and that neither method possesses, with respect to accuracy, any advantage over the other. In analysing 1 grm. of dry picrotoxine, according to their method it ought to yield, supposing it to contain 0.5 per cent. nitrogen, 5 milligrms. or 4 cub. centim. of this gas at 50°. In two analyses, made with the greatest care, the authors only obtained 0.5 cub. centim. and 0.7 cub. centim. of gas not absorbable by potash. According to this the quantity of nitrogen in picrotoxine would not amount to one-tenth per cent. In two other combustions the authors obtained 4–5 cub. centim. gas; but this consisted not of nitrogen, but of an inflammable gas. It is probably owing to this imperfect combustion that sometimes small errors occur in the determinations of nitrogen and carbon. When the anterior sixth part of the combustion-tube is filled with copper shavings, they are often seen to become quite bright during the analysis, a sign that some reducing gas is escaping. An excess of nitrogen may be obtained from the expulsion of the air contained in the potash and mercury over which the gas is collected; thus, for instance, in a bell-glass holding 400 cub. centim., which contained 100 cub. centim. solution of caustic potash and 300 cub. centim. mercury, there were evolved in the course of a short time 3–4 cub. centim. air by a current of perfectly pure carbonic acid. When the potash and mercury were employed hot, only 1 cub. centim. was expelled. It very readily happens with substances containing nitric acid, or such as have been obtained by the action of nitric acid on organic bodies, that nitrous acid is formed and passes over into the potash solution, to which it imparts a yellow colour; this inconvenience can be avoided in the following manner:—The combustion-tube, which is about 30 to 32 inches long, is filled for a length of 5 inches with bright copper turnings which have been ignited, and subsequently reduced in a current of hydrogen; behind this layer is placed a layer of finely-divided copper, obtained by reduction, and about $\frac{3}{4}$ of an inch in length; upon this follows the oxide of copper, and behind this a layer of 3 inches copper turnings or reduced copper, which however need not have a perfectly metallic surface. The end of the filled tube is connected with the gasometer-tube, and a current of atmospheric air passed through it, while the copper turnings last introduced are heated to

* I have since submitted some of the same sample of picrotoxine which served for my former analyses to Lassaigne's test, the extreme delicacy of which I can bear testimony to, and find the statement of Messrs. Erdmann and Marchand to be perfectly correct.—W. F.

redness, when they completely absorb the oxygen of the air. When now the tube is filled with pure nitrogen gas, it is gradually heated in its entire length, and thus the oxide of copper, with the copper in front of it, is ignited in a current of nitrogen, in which the metal retains the whole of its lustre; when this has been done, the fire is removed, and only the hinder portion of the copper retained at a red heat until the front portion has become tolerably cool. When the whole has become cold, the hinder partially-burnt copper is removed, the substance to be analysed conveyed into the tube by means of a long-necked flask, mixed with the oxide, and the ignited oxide of copper introduced as usual. On commencing the combustion, after the current of gas has been regulated, the finely-divided copper only is at first heated to redness. The current of gas, which in the commencement consists only of the atmospheric air which had been left on heating the tube to redness, on passing over the finely-incandescent copper is entirely deprived of its oxygen. The copper turnings are not heated to redness until they are surrounded by an atmosphere of nitrogen, upon which the combustion is proceeded with. The hindermost portion of the copper situated anteriorly is not seen to become incandescent until the combustion is complete, when free oxygen reaches it; the current of oxygen is then discontinued, and one of atmospheric air passed through the tube while the firing is removed.—*Journ. für Prakt. Chem.*, xxxvii. p. 146.

Mode of dividing Plates of Zinc. By M. WAIDELE.

It is frequently a subject of great difficulty to divide plates of cast zinc for use in galvanic batteries. The following is a simple and ready method of accomplishing this end. Grease the plate over by means of a rag and a little tallow; with a pointed instrument draw a line in the required direction of the cut, so as to remove the grease from that spot, and penetrate slightly into the metal; pass a little dilute sulphuric acid over this line by means of a feather, and then let a drop or two of mercury fall on the same spot; the zinc soon becomes amalgamated in the direction of the line, and through its entire thickness. A slight blow, properly given, will cause it to break.—*Revue Scient.*, Feb. 1846, p. 257; and *Silliman's Journal*, Sept. 1846.

On the Red Colour of the Protosalts of Manganese.
By A. VÖLKER.

Many chemists have ascribed the red colour of the protosalts of manganese to the presence of a higher oxide, and have described various methods for removing it. Thus Trommherz and Brandes advise precipitating a tolerably strong solution of a rose-coloured protosulphate of manganese by carbonate of potash, dissolving the washed protocarbonate in sulphuric acid, precipitating it again, and

repeating this operation until a colourless solution is obtained. On each solution in sulphuric acid a portion of the intermixed higher oxide is said to be converted into protoxide and oxygen, and finally to disappear entirely. Since the protocarbonate, on washing in the air, is readily oxidized higher, it is evident that the frequent precipitation is more injurious than advantageous. I shall subsequently show that, by one solution of the protocarbonate of manganese in sulphuric acid, the so-called colourless salt is obtained, when a sufficient quantity of concentrated sulphuric acid has been employed.

According to Brandes, the colourless salt is obtained when the pulverized sulphate is boiled in spirit or æther, and then dissolved in water, or when its solution is boiled with some sugar. According to Brandenburg, the colourless salt is obtained on heating to redness manganese with English oil of vitriol, and the red salt with fuming oil of vitriol. Gmelin, on the contrary, always obtained a coloured salt by igniting manganese with fuming or monohydrated sulphuric acid, which on being heated to redness and again dissolved, afforded a red solution, which could not be decolorized by sulphurous acid or continued boiling with sugar, even on the addition of sulphuric acid. He thence concludes that the red colour of the protosalts of manganese cannot be ascribed to the presence of a higher oxide. Berzelius entertains the same view, and supposes the difference of colour to depend on isomerism.

I have repeated all the above experiments, but without succeeding in obtaining a perfectly colourless salt. When protocarbonate of manganese, which has been washed exposed to the air, is heated with dilute sulphuric acid, a very red solution is obtained, while a brown powder remains undissolved; when, on the other hand, concentrated sulphuric acid is employed, a colourless solution is obtained, which on cooling solidifies to a tissue of colourless crystals. It being known that salts of manganese are very readily more highly oxidized in the presence of a superoxide and free dilute acid, as for instance peroxide of lead and dilute nitric acid, I assured myself that the red solution obtained by dissolving protocarbonate of manganese in dilute sulphuric acid, owes its red colour to an admixture of a higher oxide of manganese, for it is instantly decolorized by a few drops of sulphurous acid or an organic substance. It appeared to me beyond all doubt that the red colour was to be ascribed to a higher oxide, and that protoxide of manganese, perfectly free from oxide, yielded colourless salts; but in preparing a larger quantity of the colourless salt, by dissolving pure protocarbonate of manganese, I obtained crystals which singly appeared colourless, but in mass exhibited a decided though faint reddish tint. This slight colour could not be removed either by sulphurous acid, organic substances or sulphuretted hydrogen; it could therefore not be ascribed to the presence of a higher oxide. The protocarbonate of manganese had been prepared with care, and tested as to its purity previous to solution in sulphuric acid; the slight reddish tint could therefore not be owing to any foreign substance. I am inclined to regard this faint colouring which the protosalts of manganese exhibit, and which

cannot be removed by sulphurous acid, sulphuretted hydrogen, or any other reducing agent, as peculiar to the protosalts of manganese.

The most usual cause however of the red colour of the protosalts of manganese is owing to the presence of cobalt. In preparing the colourless salt, by treating commercial manganese with an excess of concentrated sulphuric acid, I obtained on dissolving the salt a solution, which even when largely diluted had a rose-red colour, which could not be made to disappear by sulphurous acid, or by any other reducing agent. I was long in doubt respecting this red colour, but some experiments soon showed me that it arose from cobalt; and in fact nearly all the kinds of manganese which I have examined, from the most different localities, contained more or less cobalt, some in such large quantity that it might be advantageous to obtain cobalt from them for technical purposes. I likewise found cobalt constantly present in all the red coloured salts of manganese, and the more of it the deeper they were coloured. This explains why the so-called colourless salt is obtained by heating the protosulphate of manganese to redness, since the sulphate of cobalt is readily decomposed at a red heat; it further explains why some persons have obtained colourless crystals from coloured solutions by the application of reducing substances, while others obtained coloured salts; the latter had probably employed material containing cobalt.

The separation of cobalt from manganese is readily effected in the following simple manner:—Sulphuret of ammonium, diluted with water, is carefully added in drops to the somewhat dilute solution of the salt of manganese containing cobalt, agitating constantly as long as a black precipitate is produced. The cobalt is thus completely precipitated; what first falls contains not a trace of manganese; but to be sure of removing the whole of the cobalt, it is advisable to throw down a little of the manganese with a slight excess of sulphuret of ammonium.

I am not able to confirm the statement met with in some works, that colourless salts of manganese are precipitated of a white colour by sulphuret of ammonium; at least I always obtained the characteristic flesh-coloured precipitate. The cause of this statement is undoubtedly to be ascribed to the bad nature of the sulphuret of ammonium. Sulphuret of ammonium which has been kept for a long time, and contains, owing to the frequent opening of the bottle, much carbonate of ammonia, precipitates protoxide of manganese from dilute solutions of a white colour. With ferrocyanide of potassium I obtained a white precipitate, which experienced no change even after long keeping; while the precipitate produced by ferrocyanide of potassium in the red-coloured salt containing cobalt appeared after some time reddish-brown.

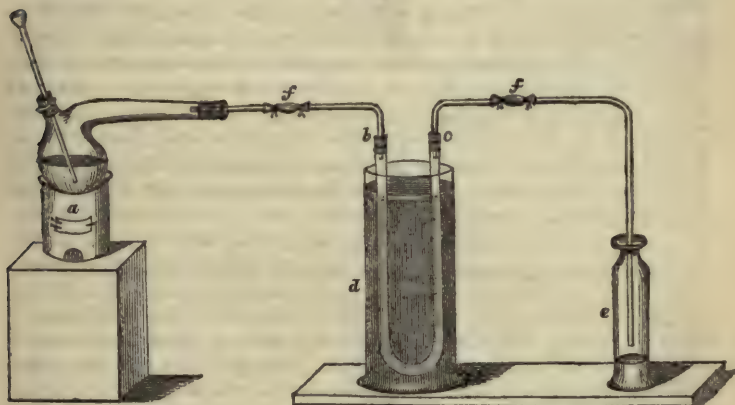
With respect to a method which has been proposed for separating quantitatively manganese from cobalt, I will cursorily observe that protochloride of manganese, according to my observation, is perceptibly volatilized when heated in a current of hydrogen gas. The hydrogen acquires the property of burning with a white luminous flame, which deposits brown stains of oxide of manganese on a cold

piece of porcelain. Water through which the gas was passed gave distinct traces of protochloride of manganese. The salt could not have been carried over mechanically, as it was used in the fused state. I have moreover obtained the protochloride of manganese sublimed in colourless, extremely light laminæ; the heat required however is very great.—Liebig's *Annalen*, July 1846.

CHEMICAL PREPARATIONS.

Wöhler's Process for the Preparation of pure Hydrocyanic Acid.

CYANIDE of potassium is prepared by fusing together 8 parts of dry ferrocyanide of potassium and 3 parts of pure carbonate of potash containing carbon (ignited cream of tartar), and 1 part of charcoal in fine powder in a covered crucible; the mass while still warm is powdered, and placed in a stoppered bottle of such a capacity that when 6 parts of water are added the bottle is quite filled*. When the cyanide of potassium is dissolved and the metallic iron is all deposited, the clear solution is poured into the retort *a*. The



retort is connected by means of a bent tube with the U-shaped tube *bc*; each arm of this tube is about 18 inches long and $\frac{1}{2}$ to $\frac{3}{4}$ of an inch wide. It is filled with small pieces of fused chloride of calcium, with the exception of the first one-third of *b*, which contains small pieces of the above-mentioned black cyanide of potassium.

This tube stands in a cylindrical vessel *d* of equal height; from the arm *c* proceeds a long and rather narrow conducting tube, bent

* The cyanide prepared by Liebig's process is less fit for the preparation of prussic acid; on account of the large amount of cyanate of potash it contains, much carbonic acid is disengaged, which renders the condensation of the acid far more difficult.

at a right, or any other convenient angle, into the vessel *e*; by means of the caoutchouc tubes *ff*, the apparatus is made more safe. When the apparatus is thus disposed, and all the junctions and corks found to be perfectly tight, the cylinder *d* is filled with ice-cold water, and the small and narrow flask *e*, destined to receive the acid, is immersed in snow or ice and salt up to the neck.

A cold mixture of equal parts of sulphuric acid and water is now poured through the funnel into the cyanide of potassium in the retort in very small successive portions; for 2 parts of the melted mass of cyanide of potassium 1 part of oil of vitriol is taken; the mass in the retort is so highly heated by this addition of the dilute acid as to begin to boil; the acid must therefore only be added at long intervals, taking care that no air enters with it. It is probable that a concentrated solution of tartaric acid would be preferable to the sulphuric acid. During the addition of the sulphuric acid a considerable quantity of prussic acid is developed, which would be carried out of the apparatus along with air; to avoid this the chloride of calcium tube is placed in cold water and the recipient in ice. When all the acid has been added, and the fluid in the retort no longer boils, the cold water is removed from the cylinder *d* by means of a siphon, and replaced with water at a temperature of 85° to 90° F. By this means the prussic acid previously condensed in the chloride of calcium tube is evaporated, and passes into the recipient *e*; at the same time the contents of the retort are brought to gentle ebullition, which is continued as long as prussic acid is disengaged. The tube *f* may be surrounded with ice also, when conveniently bent, so as to render the condensation of the acid more certain. Without the use of ice the preparation of the anhydrous acid should by no means be attempted; and even then, the operation, and all experiments with this substance, should be conducted with the greatest care and precaution.—*Handwörterbuch der Chemie*, vol. ii. p. 406.

On the Preparation of Jalap Resin. By E. SOUBEIRAN.

Four different processes have been described for preparing the resin of jalap. The Codex directs the root to be exhausted with alcohol of 0·863 spec. grav., which is then distilled, and the resin forming the residue of the distillation is washed and dried.

It has been proposed to treat the jalap with alcohol of 0·921, following in other respects the method of the Codex. Apparently the two processes should give a similar definite result, the whole of the resin being equally dissolved, and the washing separating the extractive matters, which have been taken up in greater quantity by the weak alcohol. This however is not the case; and when the alcohol of 0·863 is replaced by alcohol of 0·921, the produce is diminished; I lost in such a case one-seventh. It is therefore advantageous to keep to the prescription of the Codex.

M. Planche has described a process, which consists in exhausting the jalap by macerations in cold water, and then pounding in water; the resin adheres to the pestle; it is far less coloured than by the

ordinary process. This process can only be applied to very small quantities of root; it is impracticable with large masses, and in every case it yields but little product. This probably led M. Nativelle to modify it, taking advantage of the ingenious idea conceived by M. Planche, of removing the extractive matters by water before dissolving the resin in alcohol. M. Nativelle, after having exhausted the jalap by repeated boiling with water, treats it with alcohol of 0·901, and decolorizes the alcoholic tinctures by means of charcoal. A very slightly-coloured resin is then obtained, which appears perfectly white when reduced to the state of powder; but the great objection in this case is also the loss of a great proportion of resin. The same jalap which had yielded 100 per cent. of resin by the process of the Codex, only yielded 64 by the process of M. Nativelle. Two causes may concur in producing this result,—the strength of the alcohol employed, and the influence of the charcoal, which retains, as is known, a very large number of organic substances. It is especially to the animal charcoal that must be ascribed the decrease in the proportion of resin obtained, as on preparing it without the intervention of charcoal its quantity amounted to 75.

It is seen that the most advantageous process is still that of the Codex; it is very simple, and can be carried out by every chemist and druggist. I cannot recommend too highly to chemists to employ and prepare themselves the resin of jalap, for this resin has not sufficiently marked characters to enable us to detect readily whether it has been adulterated.—*Journ. de Pharm.*, Sept. 1846.

Preparation of Ferridcyanide of Potassium. By Dr. RIEGEL.

It has recently been recommended, in order to prevent the formation of the well-known yellowish-green body in the preparation of the red prussiate of potash, to pass the chlorine obtained from 50 grms. salt with manganese and sulphuric acid into a solution of 50 grms. of the yellow ferrocyanide in 200 grms. water. The author could not obtain any satisfactory result by this method; he therefore recommends, when the formation of the body cannot be avoided, to allow the liquid to evaporate in a very tall vessel, when the green body is constantly deposited at the bottom of the vessel, and can readily be removed mechanically by repeated recrystallization.—*Jahrb. für Prakt. Pharm.*, xii. p. 178.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Observations on the Manufacture of Artificial Ultramarine. By Prof. C. BRUNNER.

THE author endeavoured to prepare artificial ultramarine according to the method described by Gmelin; but although it is possible to

obtain tolerably useful products by this process, success is not always certain.* All the samples obtained were considerably inferior to the natural ultramarine, and exhibited a greenish tint. After numerous experiments to prepare a more beautiful article and at less expense, the author arrived at the following results:—The materials which he employs are,—1st, silica, or pure quartzose sand, which is obtained as a powder by pulverization, and lastly suspending in water; 2nd, instead of alumina the author uses potash-alum which has been recrystallized, and which is as free from iron as possible; this is converted into *alumen ustum* and preserved in a close vessel; 3rd, flowers of sulphur; 4th, finely pulverized charcoal; 5th, dry carbonate of soda. A very intimate mixture is now made of 70 parts silica, 240 burnt alum, calculated as anhydrous, 48 charcoal-powder, 144 flowers of sulphur, and 240 anhydrous carbonate of soda. The author employs for this purpose a copper flask, tinned inside, and capable of holding 2 litres, into which from 2 to 4 oz. of the mixture are conveyed along with 1 to $1\frac{1}{2}$ lb. of coarse iron shot; the whole is shaken from 5 to 10 minutes, and then passed through a fine sieve, which retains the shot. The success of the process depends on this mixture being well made, as the powder should exhibit, even under a magnifier, no difference in the colouring of the particles. A Hessian crucible is now filled with the mixture, a lid cemented to it, and the whole kept for about an hour and a half at a red heat, taking care however to avoid a higher temperature. When the operation has proved successful, the contents of the crucible form a partly greenish, partly reddish-yellow mass, which is loosely caked together, and occupies about two-fifths of its previous volume. When it is of a brownish colour and fused, the heat has been too great. The mass is now removed from the crucible, placed in a dish with water, which extracts the sulphuret of sodium, leaving behind a greenish-blue powder, which is exhausted with cold or boiling water until this no longer exhibits any trace of sulphuret of sodium. The product thus obtained is now well mixed with an equal weight of sulphur and $1\frac{1}{2}$ time its weight of dry carbonate of soda, and then burnt as above, upon which it is again heated to redness with sulphur and dry carbonate of soda, and washed very carefully until the filtered solution is no longer coloured by acetate of lead. Now when a sample of the dried powder becomes on burning of a beautiful blue, the last operation may be commenced; if not, the heating to redness with sulphur and soda is repeated once more. In general too little heat has been given in the preceding operations. The last operation consists in spreading out on a cast-iron plate a layer about 1 line in thickness of pure powdered sulphur; and upon this as much, or somewhat more, of the well-dried preparation, which has been previously passed through a fine sieve; the plate is then heated until the sulphur takes fire, allowing the sulphur to burn away entirely at as low a temperature as possible, and so that the powder scarcely exhibits incandescence. This might be best effected on a large scale by opening and closing the doors of the furnace. This operation is repeated until the powder, which

is pulverized after each burning, has acquired the most beautiful colour, which is ascertained by experiments made on a small sample. The powder on burning increases somewhat in volume, and acquires a loose, somewhat downy consistence. The quantity of ultramarine obtained from the above materials amounts to about 160 parts.

As regards the theory of the process, there is formed, on the first heating to redness of the mixture, a chemical combination of sulphur, sodium, silica and alumina, which is still but little or not at all coloured. The addition of charcoal powder on the first ignition is not essential, but prevents the fusion of the powder; in the subsequent ignitions it is unnecessary. In the second ignition of the soda and sulphur, the amount of sulphur in the compound, and probably that of the soda, is increased. The same happens on the third ignition, the colour of the powder constantly becoming of a darker bluish-green. No favourable result was obtained on attempting to substitute one for the three ignitions. The powder acquires the true ultramarine colour only after burning with sulphur; at the same time it increases from 10 to 20 per cent. in weight, according to the consistence of the powder and the mode of operation. To compare this increase with the amount of sulphur, a sample was completely oxidized by boiling with fuming nitric acid, and the filtered liquid precipitated with chloride of barium. 100 parts of the powder, not burnt with sulphur, yielded in this way 5.159 sulphur; after being burnt five times with sulphur, when the colour exhibited the greatest intensity and the increase in weight amounted to 10.16 per cent., it yielded 12.811 sulphur; so that of the total increase in weight 7.618 per cent. was due to the sulphur and 2.542 to the oxygen. Somewhat different results were obtained with other samples, because the increase in weight was not constant; the increase in the amount of sulphur however was always less than the total increase in weight.

To ascertain the composition of the compound, some of the still unburnt highly-dried preparation was stirred into a paste with muriatic acid in an agate mortar, when it disengaged sulphuretted hydrogen, and the silica separated after some time in a gelatinous state; the mass was then digested with water and filtered from the silica, the muriatic solution supersaturated with ammonia, the precipitate collected on a filter and ignited. Muriatic acid dissolved the ignited precipitate, with the exception of a very small quantity of silica. The solution, poured into a warm solution of potash, gave a precipitate of peroxide of iron, while the alumina remained dissolved. The ammoniacal solution was digested with oxalate of ammonia, and the precipitate likewise separated by filtration. The liquid was now evaporated to dryness with some sulphuric acid, and finally heated to redness with the frequent addition of carbonate of ammonia. The residuary sulphate of soda left on solution a little silica; no potash could be detected. The analysis yielded—

	Before burning.	After burning.
Silica	35·841	32·544
Alumina	27·821	25·255
Lime	2·619	2·377
Peroxide of iron	2·475	2·246
Sodium	18·629	16·910
Sulphur	5·193	11·629
Oxygen	7·422	9·039

Now if, in the second case, the oxygen be divided between the sulphur and the sodium, we obtain, instead of the last three constituents, 20·157 sulphate of soda, and 17·421 sulphuret of sodium; so that the latter may therefore be regarded as a monosulphuret. However, the sulphur may also be combined with the lime or iron.

If, after the ultramarine has acquired on burning its most beautiful colour, this treatment be continued, we at last reach a point when no further increase in weight occurs. If it be further heated, without the addition of any sulphur, the weight decreases and the colour becomes paler, frequently with a faint tint of lilac. At the same time the powder loses its loose downy consistence, and becomes, though not always, more granular and dense. A sample of ultramarine thus modified disengaged no sulphuretted hydrogen on treatment with muriatic acid. The decrease in weight may be explained, by admitting that, while a portion of the sulphur is burnt away, the eliminated soda combines with the silica, so that only less oxygen need be absorbed. The next point to be ascertained was, whether the presence of lime, iron and sodium is essential. When ultramarine was prepared without any addition of lime, the samples turned out equally beautiful. The same was the case when materials perfectly free from iron were employed; moreover a very beautiful artificial ultramarine by Guimet, and likewise a sample of genuine ultramarine procured from Rome, exhibited not a trace of iron. A large amount of iron probably diminishes the beauty of the colour*. The author lastly employed carbonate of potash instead of soda, but the mass obtained was almost white, and on burning with sulphur did not acquire the least blue colour, although it disengaged an abundance of sulphuretted hydrogen on treatment with muriatic acid. This also appears to prove that the blue colour is not produced by the iron, but by the soda. Prückner, whose process was communicated in a former number of this Journal (vol. iii. p. 238.), considers the iron to be essential.

Erdmann has attempted to give a blue colour to the colourless or very pale-coloured haüyne by burning it with sulphur, which however proved unsuccessful, owing probably to the compact state of aggregation of the mineral; nor could the pale kinds of the Meissen ultramarine be improved by burning with sulphur; on the contrary, they lost their beautiful colour. Probably these paler kinds are

* This indeed has been found to be the case by some manufacturers in this country.—*Ed. Chem. Gaz.*

mixtures of the blue compound with colourless substances. In three analyses of Meissen ultramarine No. 1, there were found 43·77, 43·38 and 43·50 per cent. silica, 25·5–25·7 alumina, and 0·8–0·9 per cent. iron; there was but a very small quantity of lime present, and of soda about 20 per cent. Ultramarine No. 3, of a much paler colour, afforded 49·6–50·0 per cent. silica, 26·54 alumina, 1·09 per cent. oxide of iron, 0·9–1·4 lime, and 12·30–10·04 per cent. soda.—Poggendorff's *Annalen*, lxvii. p. 541; and *Journ. für Prakt. Chem.*, xxxviii. p. 128.

Manufacture of Lucifer-Matches without Sulphur. By R. BÖTTGER.

The author recommends the following composition for the preparation of lucifer-matches:—4 parts phosphorus, 10 parts nitre, 6 parts gelatine, 5 parts red lead or ochre, and 2 parts smalt. The gelatine is soaked in a small quantity of water for 24 hours, the jelly conveyed into a mortar and warmed until it has melted, when the other ingredients are introduced, constantly applying heat, but not above 167°, until the whole forms a perfectly homogeneous mass, which cannot be drawn out into threads. To make lucifer-matches with this mass, which continue to burn after ignition, without any coating of sulphur, the extremities of the matches are held for a few seconds against a plate of iron, in order to carbonize them superficially; they are then dipped into very hot melted wax, the excess shaken off with a jerk of the arm, and dipped into the above composition.—*Phys. und Chem. Vorlesung*, p. 105.

Amalgamation of Wrought Iron, Cast Iron and Steel, so as to prepare them for Fire-gilding. By R. BÖTTGER.

Place in a glazed earthenware or porcelain vessel, 12 parts by weight of mercury, 1 of zinc, 2 of sulphate of iron, 12 of water, and $1\frac{1}{2}$ of hydrochloric acid of 1·2 spec. grav.; then introduce the iron or steel into the mixture, which is to be heated to ebullition. In a little time the objects become covered with a thin coating of mercury, which enables us to apply immediately the amalgam of gold that is used in the gilding. All that is now necessary is to apply a strong heat, which will drive off the mercury and the trace of zinc that may have attached itself to the iron, leaving a surface of pure gold. By the ordinary way it becomes necessary to cover the iron first with a coat of copper.—Poggend. *Ann.*, No. i. 1846; and Siliman's *Journal*, Sept. 1846.

Artificial Marble.

M. Bouisson has taken out a patent for preparing artificial marble from gypsum, which is to be cut of the required size, placed in a metallic trough in a furnace, and kept at the temperature of 90° for some time, after which a solution of alum in boiling water is poured

upon it, and a gentle heat continued for some length of time, the water being renewed as it evaporates. For a block 6 feet long and 2 feet in the other directions, exposure for 5 hours before the addition of alum solution, and 72 hours after, suffices to impregnate the plaster. The strength of the alum solution is 1 lb. to 6 quarts of water. It is always well to cut the plaster in the form required before hardening it. By introducing colouring matter into the solution various tints may be obtained.—*Journ. de Chem. Méd.*, April 1846; and Silliman's *Journal*, Sept. 1846.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Southampton, Sept. 10, 1846.

THE following are abstracts of some of the principal communications read before the Chemical Section, as reported in the *Athenæum* and *Literary Gazette*:—

On the Decomposition of Water into its Constituent Gases by Heat.
By Prof. W. R. GROVE.

Mr. Grove first asserted, probably to the surprise of those in the habit of using the eudiometer, that every process that will combine gases can separate them. He was led to this result from the use of the eudiometer invented by him, which he briefly described, and by means of which he could apply intense heat to limited quantities of gases, analyse even a bubble most accurately, or produce any effect of eudiometry, also decompose and analyse camphor, &c. Before proceeding to the experiments, he mentioned one point in relation to equivalents which he considered worthy of attention. It was, that hydrogen, as pure as it could be obtained, when passed into the glass tube of his eudiometer, and submitted to the intense heat of the platinum wire, contracted in volume. This he found to be due to a mixture of oxygen with the hydrogen; and whatever pains he took, the hydrogen was never entirely free from oxygen. Experiment proved this beyond a doubt. But the facts he observed with the first and immediate reference to the discovery of the decomposition of water by heat alone were, that two volumes, one each of hydrogen and carbonic acid, exposed to the heated platinum wire, contracted into one volume, the residue being carbonic oxide; and that carbonic oxide, similarly exposed over water, expanded to one-third of its volume, this expansion being permanent, the carbonic oxide taking oxygen from the water and becoming carbonic acid. Here then were instances of oxygen being taken by hydrogen from carbonic acid leaving carbonic oxide; and oxygen taken from hydrogen by carbonic oxide, producing carbonic acid; an apparent case of the reversion of chemical affinity. If this were the case, Mr. Grove thought, as heated platinum wire combined oxygen and

hydrogen to form water, it should also decompose water and give off these gases. And this he eventually succeeded in accomplishing; first he obtained a grain bubble only, but afterwards a current of gas, the platinum wire being heated as nearly as possible to the point of fusion by the electric battery. In order however to remove every doubt as to the possibility of the electrical action of the battery being concerned in the decomposition, he arranged an apparatus in which the heat of the blowpipe could be employed, and the same results were obtained, proving to his satisfaction that water was decomposed by heat alone.

On the Rationale of certain Practices employed in Agriculture.
By Prof. DAUBENY.

The Professor's paper referred chiefly to the use of quicklime and of gypsum as fertilisers to the land. The former of these substances he supposes to act in part, by rendering those inorganic substances which are present in the soil more soluble; or, in accordance with the views laid down by the author in a memoir which he has published in the 'Philosophical Transactions' of last year, by converting the *dormant* constituents of the soil into active ones, or into a state in which they become immediately available. He appealed to the authority of Prof. Fuchs, confirmed by that of Mr. Prideaux of Plymouth, as showing that the alkali may be extracted from granite readily by water after the rock in a pounded form has been heated together with quicklime; and he stated that a soil exhausted by long-continued cropping was found by himself to yield to water twice as much alkali after having been mixed with quicklime as it had done before. Hence the frequent application of lime tends to produce exhaustion in the land; not only because it supplies in itself no fresh alkali, but likewise because, by rendering that which the soil contains more soluble, it causes it to be washed away more readily by atmospheric water. Ploughing, and other mechanical methods of pulverizing the soil, appear to act in the same way; and so also may we suppose to do the sprinkling of the soil with sulphuric acid, as is practised in some parts of the Continent. The author then alluded to the various modes of explaining the advantage attributed to gypsum, which certain leading agricultural chemists had proposed; one ascribing its virtues to the direct influence of the salt; another to the indirect good resulting from it, owing to its property of fixing ammonia; a third regarding its acid constituent as of the principal utility; and a fourth its base. Dr. Daubeny gave reasons for rejecting the third and fourth of these hypotheses; but considered that the use of gypsum may be in part attributable to the first, and in part to the second, of the causes pointed out. He supposes that this substance is generally useful to all plants from its property of fixing ammonia, and also especially serviceable to certain species by supplying them with a salt which they require for their development. He was principally anxious however to bring forward this subject, in the hope of inducing chemists to institute experiments for the purpose of setting the question at rest.

On the Action of Oxalic Acid upon the Blood and Dead Tissues of the Animal Body. By Dr. LETHEY.

It has been stated by Dr. Coindet, Dr. Christison and others, that oxalic acid does not appear to have any corrosive action on the stomach like the mineral acids. Dr. Letheby however remarks that these statements are opposed to the observations which he has made. In every case which he had examined of poisoning by oxalic acid, the stomach after death was found to be so completely corroded that it would not hold together. Numerous experiments were made with various animal tissues, such as submitting skin, stomach, intestine, muscle and tendon to the action of oxalic acid of different strengths. After standing about 12 or 14 hours at a temperature of 60° F., it was found that the cellular and mucous tissue of each underwent either complete solution, or else was so softened that it broke down under the pressure of the thumb and fingers; the albuminous and muscular tissues were also softened, and looked as if they had been scalded. The solutions were then filtered and evaporated in a water-bath; by which means a gelatinous-looking mass was obtained, and the oxalic acid had so entered into combination with the gelatine that it could not be dissolved out in its usual manner by the action of cold alcohol.

Notice of a Gas Furnace for Organic Analysis. By Dr. PERCY.

This was an ingenious arrangement, by which gas, burnt, mixed with air, through wire-gauze, was substituted for charcoal. Its advantages are its extreme cleanliness, and the power which the operator possesses of regulating at will the heat, which, according to the author, is not practicable in the ordinary furnace for organic analysis with charcoal.

Comparative Analytical Researches on Sea Water.

By Prof. FORCHHAMMER.

In the ocean between Europe and America the greatest quantity of saline matter is found in the tropical region, far from any land; in such places 1000 parts of sea water contain 36·6 parts of salt. This quantity diminishes in approaching the coast, on account of the masses of fresh water which the rivers throw into the sea; it diminishes likewise in the westernmost part of the Gulf-stream, where I only found it to be 35·9 in 1000 parts of water. By the evaporation of the water of this warm current, its quantity of saline matter increases towards the east, and reaches, in N. lat. 39° 39' and N. long. 55° 16', its former height of 36·5. From thence it decreases slowly towards the north-east; and sea water, at a distance of from 60 to 80 miles from the western shores of England, contains only 35·7 parts of solid substances; and the same quantity of salt is found all over the north-eastern part of the Atlantic, as far to the north as Iceland, always at such a distance from the land that the influence of fresh water is avoided. From numerous observations made on the shores of Iceland and the Faroe Islands, it is evident that the water of the Gulf-stream spreads over this part of the

Atlantic Ocean; and thus we see that the water of tropical currents will keep its character even in high northern latitudes. In the longitude of Greenland, and more than 100 miles to the south of the southernmost point of that large tract of land, sea water contains only 35 parts of saline matter in 1000 parts. In going from this point towards the north-west it decreases constantly; and in Dover Straits, at a distance of about 40 miles from the land, it only contains 32·5 parts of salt in 1000 parts of water. This character seems to remain in the current which runs parallel to the shores of North America, and at N. lat. $43\frac{1}{2}^{\circ}$ and N. long. $46\frac{1}{3}^{\circ}$ the sea water contained only 33·8 parts of salt. Thus tropical and polar currents seem not only to differ in respect to their temperature, but also in the quantity of salt which they contain; and thence it follows again, that while the quantity of water carried away from the *tropical sea* by evaporation is greater than that which rain and the rivers give back to that sea, the reverse takes place in the *polar seas*, where evaporation is very small and the condensation of vapour very great. The circulation must on that account be such, that a part of the vapour which rises in tropical zones will be condensed in polar regions, and in the form of polar currents flow back again to warmer climates. Although my analyses are only made on water from the ocean between Europe and America, yet little doubt can be entertained that also that part of the ocean which separates America from Asia is in a similar condition; and that currents flowing from the poles are the rule, and currents flowing towards the poles the exception. Besides the southerly direction, which any current flowing from the northern polar regions must take, it will, according to well-known physical laws depending upon the rotation of the earth, always take a direction towards the west, and thus be driven towards the eastern shores of the continents; while any tropical current flowing towards the north will, according to the same laws of rotation, take a direction towards the western shores of the continents. This is at present the case in the Atlantic Ocean; and its effects upon the shores of Europe, which are surrounded by warm water by a branch of a tropical current, produce a mild and moist climate. The water of the different seas is much more uniform in its composition than is generally believed. In that respect my analyses agree with the newer analyses of atmospheric air in showing that the differences are very slight indeed. Sea water may contain more or less salt; from a very small quantity, as in the interior part of the Baltic, to an amount of 37·1 parts in 1000 parts, which I found in water from Malta, and which is the greatest quantity I ever observed; but the relative proportion of its constituent saline parts changes very little. In order to get rid of those differences which might arise from the different quantity of saline matter in sea water, I have compared sulphuric acid and lime with chlorine, and the following results are the mean of many analyses:—In the Atlantic, the proportion between *chlorine* and *sulphuric acid* is 10000 to 1188; this is the mean of 20 analyses, which differ very little from each other. In the sea between the Faroe Islands, Iceland and Greenland, the same proportion, according

to the mean of 17 analyses, is 10000 to 1193. In the German Ocean, according to 10 analyses, it is 10000 to 1191. In Davis's Straits, according to the mean of 5 analyses, it is 10000 to 1220. In the Kattegat, according to the mean of 4 analyses, 10000 to 1240.

Thus it appears that the proportion of sulphuric acid increases near the shores; a fact which evidently depends upon the rivers carrying sulphate of lime into the sea. The proportion between *chlorine* and *lime* in the Atlantic Ocean, according to the mean result of 17 analyses, is 10000 to 297; and in the sea between Faroe and Greenland, according to the mean of 18 analyses, 10000 to 300. Lime is rather rare in the sea around the West Indian Islands, where millions of coralline animals constantly absorb it, the proportion, according to 5 analyses, being 10000 to 247; and it is rather copious in the Kattegat, where the numerous rivers of the Baltic carry a great quantity of it into the ocean. The proportion is there, according to 4 analyses, 10000 to 371.

On the Changes which Mercury sometimes suffers in Glass Vessels hermetically sealed. By Prof. ØERSTED.

It has been frequently noticed that mercury inclosed in glass tubes, even when those tubes are hermetically sealed, undergoes a remarkable change. It first becomes covered by a thin film of a yellow colour, which adheres to the glass, and becomes eventually nearly black. This has been attributed to oxidation; but the oxidation which would arise from the exceedingly small quantity of atmospheric air which could be contained within the bulbs exhibited by Prof. Oersted was too small to account for the formation of such a quantity of dark and yellow powder as many of them exhibited. Prof. Oersted referred the change on the mercury to the action of that metal on the glass of which the bulb was formed. It appears that sulphate of soda is frequently employed in the manufacture of glass, and it is thought that a sulphuret of mercury is formed by the decomposition of the glass itself. This is not however proved, and it has only been brought forward that attention might be directed to a subject which appeared to involve some remarkable conditions.

On the Difference in the Physiological Actions of the Yellow and Red Prussiates as an Evidence of their containing dissimilar Radicals. By Dr. LETHEY.

In the course of my inquiries into the actions of the various compounds containing cyanogen on the animal economy, I was particularly struck with the great dissimilarity in the effects produced by the yellow and red prussiates of potash. This led me to think it might furnish some evidence upon the side of Liebig's doctrine, that the two salts contain radicals which are dissimilar. To prepare myself for this inquiry however I thought it necessary to ascertain what would be the effects of the simple and the double cyanides, and then to experiment with the yellow and red prussiates of similar bases. Of the simple cyanides I chose those of potassium, sodium, ammo-

nium, mercury, lead, iron, zinc and silver; and to provide against any fallacy which might arise from the action of the gastric juice, I injected them into the veins or peritoneal cavity. Contrary rather to my expectations, it was found that they were all poisonous; the soluble ones generally acting as quickly as prussic acid, while the others required a little longer time for the development of the symptoms; but in all cases death followed their administration, from 2 to 5 grs. being sufficient to produce such a result. Of the double cyanides I chose those of potassium and zinc, potassium and silver, potassium and nickel, and a mixture of cyanide of potassium with cyanide of iron. These also were found to be most poisonous, proving fatal in doses almost as small as the preceding. Now these inquiries clearly established two facts, that neither the simple nor double cyanides could be given even in 5-grain doses with impunity. How great therefore was my astonishment to find that a class of salts regarded by some chemists as double cyanides should have little or no action upon the animal economy, and that they might be administered in doses of half an ounce without their exhibiting any unpleasant symptoms whatever! I am alluding now to the ferrocyanides; and I experimented with those of potassium, sodium, ammonium, barium, lead, iron and silver. Moreover, I am disposed to think that the acid called by Liebig ferrocyanic, which I liberated both by the action of muriatic acid and æther on the potassium salt, and by that of sulphuretted hydrogen on the ferrocyanide of lead, was equally inert. It was true that when the acid was injected into the peritoneum it produced a slow poisoning, but the effect was evidently due to its decomposition and to the liberation of hydrocyanic acid; for this compound was easily detected in the abdominal cavity directly after death. I next examined the effects of the red prussiates; and here again, contrary to what would have been surmised from the want of action in the preceding compounds, it was found that they constituted a class almost as poisonous as the simple cyanides. My experiments were made with the red prussiates of potash and lead, and with a crystalline acid which I obtained by the action of muriatic acid and æther upon the former of these compounds; each of these was quickly fatal in doses of from 10 to 40 grains.

PATENT.

Patent granted to James Laming, London, for Improvements in making the Cyanides and Ferrocyanides of Potassium and Sodium.

THE patentee, before describing the invention as communicated to him from abroad, has, for the better understanding of the improvements, detailed the chemical facts or principles upon which they are founded. These are as follow:—

1. When animal matter, which contains nitrogen as well as hydrogen and carbon, is exposed to a high temperature, not exceeding

low red, an equivalent of nitrogen combines with 3 equivs. of hydrogen to form an equivalent of ammonia, and the carbon is separated.

2. When ammonia is exposed to carbon at a full red heat, an equivalent of ammonia exchanges 2 of its equivalents of hydrogen for 2 equivs. of carbon, and thus becomes prussic or hydrocyanic acid.

3. If free potassium or sodium be also present, the equivalent of ammonia parts with all its 3 equivs. of hydrogen, and the nitrogen which remains takes in their place 2 equivs. of carbon to form cyanogen, and 1 equiv. of potassium or sodium, as the case may be, to form a cyanide of the metallic base.

4. When animal matter is exposed to heat, its temperature becomes gradually increased to low redness before it assumes that higher temperature indicated by a full red colour; therefore whenever animal matter is subjected to what is called destructive distillation, the formation of ammonia must take precedence, in point of time, to that of prussic acid or of the cyanides.

5. When the oxide of potassium or of sodium, or the carbonate of either of those oxides, is intimately mixed with carbon, and exposed to a heat approaching to whiteness, its metallic base is set free from the oxygen with which it was previously combined, and rises in vapour. If ammonia comes into contact with the mixture of carbon and alkali, or of carbon and alkaline carbonate, the separation of the metallic base from its oxygen takes place at a lower temperature, under such circumstances a full red heat being sufficient. In the case of the carbonates, the metallic bases, potassium and sodium, are liberated from the carbonic acid also whenever they separate from their oxygen.

6. Cyanide of potassium or cyanide of sodium, by exchanging an equivalent of every 3 equivs. of its base for an equivalent of iron, is converted into the corresponding ferrocyanide, or what is called in commerce prussiate of potash or prussiate of soda; and this change may be effected by causing the cyanides of the respective metals dissolved in water to come into contact with iron or oxide of iron in a state of division.

The ordinary way of combining potassium or sodium with cyanogen, preparatory to making the prussiate of potash or prussiate of soda for commerce, is to expose in iron pots an impure carbonate of one of those alkalies and animal matter to a red heat, and to trust for the necessary contact of the nitrogen and carbon of the animal matter with the metallic element, to the thorough incorporation of the ingredients of the pasty mass by stirring. While the temperature of the animal matter is approaching redness, ammonia is constantly being generated, and as it is volatile it escapes and is lost; and this is continued until the heat becomes great enough to convert the nitrogen and carbon of the animal matter into cyanogen, and to fix that cyanogen by combining it with the metallic base of the alkali. Another source of loss is the difficulty of causing the different elements contained in the pasty mass to combine; for be-

fore each can be brought into contact with the other by mechanical agitation their temperature becomes elevated, and great part of the resulting nitrogenous gases, which are volatile, have time to escape. There is a third evil attending the ordinary process, namely the proportion of carbon in animal matter compared to its nitrogen is greater than that in the alkaline cyanides; the greater part of this carbon, from its fixed nature, remains to solidify the mass from which the nitrogen so freely escapes; so that it becomes necessary to suspend the addition of the animal matter, on account of the mass being too solid for the chemical action to go on before enough of nitrogen has been combined to convert much of the alkali into prussiate.

Two patents have already been granted for methods of preventing the losses sustained in the ordinary way of making the prussiates of potash and soda. By one of these methods the ammonia which is liberated from a heated mixture of alkali and animal matter is conducted first over the surface of fused alkali (the said alkali having no admixture of carbon), and afterwards into a vessel containing a solution of alkali. The other of these methods directs that the ammonia, which results from animal matter exposed to heat, be made to pass upwards and downwards through a series of vertical pipes, arranged on the principle of inverted siphons, heated to redness, and charged with a mixture of charcoal, potash and iron, reduced to small fragments. With regard to the former of these methods, it is well-known to chemists that fused alkali has no power of decomposing ammonia into cyanogen unless carbon be present; and with regard to the latter method, it is obvious that, as the materials, if brought into a state of fluidity or pastiness, must of necessity choke the passage of the pipes, the method demands that the mixture in the inverted siphons be kept from losing its solid or granular state; and the continuance of that state is secured by the large proportion of infusible charcoal compared to the fusible potash, which the patentee prescribes, as fulfilling his intentions in a satisfactory manner.

Now under the present invention the patentee makes use of charcoal, or other form of carbon, in powder, mixed with one of the alkalies, or its carbonate or other salt capable under the circumstances of surrendering its metallic base to cyanogen. This mixture is constantly maintained in a fused state, so as to be fluid, or at least in a pasty condition, which is highly favourable for converting the metallic base of the alkali or its salt into a cyanide, and which takes place rapidly under such circumstances when a current of ammonia gas is introduced to the fused mixture. The metallic base of potash or soda, or of their compounds respectively, as the case may be, is liberated by the agency of the heated carbon, assisted by the affinity of the metallic base for the cyanogen, which is at the same time formed by the combination of heated carbon with the nitrogen of the ammonia; cyanide of the metallic base is thus produced, and this product is constantly augmented in quantity (the current of ammonia being continued) until great part of the alkali,

or other compound of its base, has become converted into cyanide. When an alkaline carbonate is used, powdered charcoal, to the amount of more than 30 per cent. of its weight, may be added without destroying the fluidity of the mixture if the temperature is raised to a full red. When the potash or soda is in a caustic state, a larger proportion of charcoal may be added; or, what is more advantageous, the mixture will remain fluid, although the heat be raised not so high. Whether the ammonia gas is passed through the mixture of carbon and fused alkali, or other compound of its metallic base (which is preferred), or over its surface, it is better to have more than one vessel charged with the heated materials, and so connected together by pipes, that the nitrogen of the ammonia, which escapes the chemical reaction in the first vessel, shall not pass through the whole series without combining. The apparatus thus acts on the principle of a series of Woulfe's bottles; and according to this invention all the vessels are made red-hot except the last, into which water, or some liquid convenient for arresting the vapours of alkaline metal, is put; or otherwise the vapours might be lost. The first product, as in the common process for making prussiate, is a cyanide of the alkaline metal present, which may be dissolved out from the mass, technically called "metal," by boiling the latter in alcohol of about 0.896 spec. grav., from which filtered hot it spontaneously separates in great part on cooling. To obtain the ferrocyanide, the metal is to be treated in the usual way, namely, its soluble parts dissolved in water, then treated with iron, the solution evaporated, and when sufficiently concentrated and clear set aside to crystallize; and the rough product is afterwards purified by recrystallization.

The patentee states, that he does not claim the invention of any process for dissolving out or obtaining either cyanide or ferrocyanide from the compound termed "metal;" nor does he claim the construction of apparatus wherewith the process or processes may be carried on; but he describes some arrangements which have been found to answer. One of these consists of three iron air-tight covered pots, communicating with one another in the manner of ordinary Woulfe's bottles; that is to say, the induction-pipe of the first pot reaches to near its bottom, its eduction-pipe reaches down the interior of the second pot to near its bottom, and the eduction-pipe of this second pot terminates in like manner in the third pot, while the eduction-pipe of the latter plunges beneath the surface of some water or other liquid convenient for oxidizing and arresting vapours of alkaline metal. Each of the pots has a man-hole in its cover, by means of which it may be charged and discharged, and a door by which it may be perfectly closed. Each covered pot is so set in a furnace as to be heated to a temperature great enough to keep its contents in a state of constant fusion. Its charge when fused should about half fill it. By the use of this apparatus, the ammonia which is forced into the first pot, by reason of its own elasticity under the pressure attending its assumption of the gaseous state, passes through the fluid mixture of fused alkali and carbon in

that pot, being there decomposed into nitrogen or cyanogen, and as cyanogen combining with and saturating the alkaline metal present; after which the ammonia or its nitrogen or uncombined cyanogen, which results from its action on the carbon still remaining in that pot, passes into the second pot, to convert the alkaline metal there present into a cyanide. In like manner the ammonia or its nitrogen, or the resulting cyanogen, may arrive in the third pot; then is the time for stopping the operation, in order that the first two pots may be emptied and recharged. Owing to the volatility of the alkaline metals at high temperatures, the pipes of communication between the pots are apt to become obstructed; for this reason they are proposed to be made straight, and joined together at right angles, in such a manner, that by removing a screw-plug from the end of each rectilinear piece, the passage through it may be cleared by passing into it a short rod of iron; in order that this process need not be often repeated, the diameter of the pipes should be as great as convenience admits of.

The patentee next describes a modification of the preceding apparatus, wherein no pressure is required to overcome the resistance opposed to the current of ammonia by the fluid mass into which the induction-pipes of the preceding apparatus are immersed. In this modification all the induction-pipes stop short at the covers of the pots except that of the open pot, which may be allowed without much inconvenience to dip below the surface of the water, or other liquid intended to arrest the metallic vapours.

The ammonia gas, in this case urged forward by an inconsiderable amount of pressure, comes into contact with the surfaces of the fused ingredients in the several pots in succession, until it is either decomposed and its nitrogen absorbed, as in the preceding case, or escapes by the last induction-pipe of the series; to prevent which, either the number of pots may be increased, or, what is better, each of the three should be furnished with agitators moved by machinery or labour. When the latter arrangement is adopted, each pot should be furnished with a lofty conical cover, containing at its apex a stuffing-box, in which the axis of the agitator turns, and which is kept sufficiently cool by a stream of water running through a small cistern, which embraces the stuffing-box. With this apparatus the fused ingredients may be either in a fluid, semi-fluid or pasty condition.

The patentee claims the making of the cyanides and ferrocyanides of potassium and sodium, or, as they are called in commerce, prussiates of potash and soda, in any suitable apparatus, by passing ammonia (either pure or mixed with such other gases as do not prevent the desired result) over the surface or through the mass (according as the induction-pipes may dip or not below the surface) of potash or soda, or other compound of potassium or sodium (capable under the circumstances of setting free its metallic base), in a state of fusion by heat, and mixed with charcoal, or other form of carbon in powder, and in such proportion as to be adequate to effect, without destroying by its bulk, the fluid, semi-fluid, or pasty condi-

tion of the resulting mass. And further he claims, for the process or processes of this invention, the sole use of ammonia, or mixture or combination of ammonia with other gases or vapours, whatever be the source from which it is obtained, provided always that in such mixture or compound there be no substance present capable by its nature of preventing the desired result. He claims, for example, the application to this invention of ammonia or carbonate of ammonia obtained from gas-water, from urine, from the liquor condensed in the distillation of bones or other animal matter, or from one or other of the salts of ammonia, or a solution of ammonia; and also the ammonia or carbonate of ammonia which is obtained directly mixed with other gases in the carbonization of bones and other animal matters, and in the chemical treatment of guano. Whatever be the source from whence the ammonia is obtained, it is desirable that it should be made as free from the vapour of water as possible before it is introduced to the fused materials; for this purpose the substances from which it is to be eliminated may be dried, or else the ammonia may be passed in an elastic state in contact with some substance known to chemists to be convenient for desiccating that gas.

Instead of obtaining the ammonia by a separate process or from a distinct vessel, the inventor sometimes causes it to be given off from animal matter contained in the vessel or vessels in which the cyanide is formed. For this purpose it is better to use the potash or the soda in a caustic state, causing it while in that condition to dissolve the animal matter. The following is the mode of proceeding:—A caustic solution of alkali, in water or other convenient liquid, is first made boiling-hot, and to it while boiling as much animal matter is added as it will readily dissolve; the solution is next evaporated to dryness, and the mass preserved in that state for use. When a portion of this mass is put into each of the heated vessels except the last, of such a series as has been described, and the last heated vessel is charged with carbon, mixed with some convenient compound of an alkaline metal, as before stated; then the ammonia, which escapes from any one of the vessels in the series, will have to pass through one or more subsequent vessels, and thus tend to suffer decomposition, the resulting nitrogen being converted into cyanogen, and then being absorbed. This admits of the cheaper kinds of animal matter being used, such as the undried flesh and viscera of carrion, and old woollen flock and rags, which, by reason either of humidity or too great volume, cannot conveniently be mixed in their natural state with red-hot alkali. The patentee claims this modification of the process as part of the invention for which this patent has been granted. Sometimes the mass resulting from the desiccation of the solution of animal matter in caustic alkali is put into red-hot open pots; in this case much ammonia is lost; but the improvement which is introduced by replacing the ordinary mechanical mixture by an intimate chemical combination, affords a greater product in prussiate than can be obtained from an equal quantity of animal matter treated in the ordinary way.—Sealed Nov. 18, 1845.

THE CHEMICAL GAZETTE.

No. XCVII.—November 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Colour of the Blood. By Dr. R. F. MARCHAND.

VAN MAAK was the first to connect the alteration in the colour of the blood with the oxidation of the iron; supposing that the cruor which contained carbonic acid was oxidized and freed from carbonic acid by oxygen. But Mulder has proved that the iron may be removed from the hæmatine without the latter losing its red colour; and moreover, that it neither exists as protoxide nor peroxide, but in the metallic state, in the hæmatine, because this yields with sulphuric acid a solution of the protoxide, hydrogen being evolved at the same time. Dumas regards the blood-corpuscles as living beings, which have their own respiratory function, and the sum-total of which constitutes the respiration of the animal. Some time ago* the author proved that oxygen does not exert any action, made manifest by the evolution of carbonic acid, upon the blood when removed from the body. According to the view of Dumas, it might appear that the blood-corpuscles, as formerly treated by the author, were already dead, and hence could not exert any chemical influence. Perfectly fresh sheep's blood therefore was instantly beaten, placed whilst still warm in a saturated solution of sulphate of soda, and rapidly filtered. During the filtration the funnel was kept at a temperature of 97° F., washed with a concentrated solution of sulphate of soda at the same temperature, and a continuous current of oxygen gas passed into it from six tubes which were deeply immersed. Towards the end of the filtration the serum which passed through was coloured, and the layer of blood-corpuscles close to the filter had become dark red, not from any chemical change, but merely from a more dense aggregation of the particles. The blood-corpuscles were placed in a flask with the saline solution, and treated with a current of oxygen which had been washed with solution of potash; but no trace of carbonic acid could be detected by barytic water in the 20000 cubic centimetres of gas which passed through. In a second experiment the blood was placed in the apparatus two hours only after having been drawn, but no carbonic acid was evolved even in this case. This however by no means proves that

* Chem. Gaz., vol. iii. p. 511.

the oxygen may not exert some action upon the blood in the organism; but it remains to be ascertained whether the change in the blood without the body arises from physical or chemical causes. As we know, mixed blood is rendered of a beautiful bright red colour by oxygen gas, and by carbonic acid dark red. These colours are less distinct if arterial or venous blood be caught separately. Arterial blood always contains carbonic acid, venous blood always contains oxygen; if the two kinds of blood be continuously shaken with one gas only, the foreign gases are perfectly separated, and its isolated action is seen. If blood which has been saturated with carbonic acid be placed under the air-pump, it gives up part of its carbonic acid, and becomes of a brighter colour; blood which has been saturated with oxygen, under the air-pump loses oxygen and becomes of a darker colour. In neither case could any difference be perceived with the microscope in the form of the corpuscles. The same action is exerted upon blood charged with oxygen by the air-pump as by the transmission of hydrogen and nitrogen; hence we need not admit that any reduction of the blood is effected by them. If the oxygen were in a condition for forming carbonic acid in the blood, blood which has been reddened by it would occasionally become darker from the carbonic acid formed, which however only occurs on incipient putrefaction. It follows from these facts, that the alteration in the colour of the blood produced by the above gases is mechanical, even though not produced by alteration in the form of the corpuscles. Magnus has well compared the phenomenon to the reaction of the nitrous oxide gas on solution of protosulphate of iron.

If blood be mixed with twice its volume of water, it becomes very dark. The corpuscles are deprived of their colouring matter, and apparently dissolve. If the blood had been agitated with oxygen, air, hydrogen or carbonic acid, before the mixture with water, we find no difference, by transmitted light, between the action of hydrogen and carbonic acid, nor oxygen and air. The froth of blood which has been shaken with hydrogen is brighter than that treated with carbonic acid. Blood which has been shaken with oxygen is lighter by candlelight than that which has been shaken with air.

Blood, after mixing with water, when agitated with carbonic acid, by long repose continues to become brighter at the margin, evidently from the action of the oxygen of the air. If a dark aqueous solution of blood be agitated with air, it becomes bright and transparent, as also when a current of air or oxygen gas is passed through it. Scherer thinks that this is also caused by carbonic acid, but this is incorrect. If a mixture of carbonic acid with one-sixth of oxygen be used, this acts in the same way as pure oxygen, and even with one-twentieth part of oxygen a distinct brightening occurs; it is therefore possible that Scherer used impure carbonic acid. If this clear solution of blood be agitated with carbonic acid or hydrogen, it becomes darker, and finally opaque by daylight, but it never becomes brighter and clear. As regards the effect of salts upon the colouring matter of the blood, the colour produced by sulphate of

soda is decidedly of a more scarlet red than that by oxygen. The action of this salt is to be explained in the same way as in the case of finely divided precipitates, for instance sulphate of baryta, which likewise does not pass through the filter as long as the solution contains a certain amount of muriate of ammonia, &c. Blood, when saturated with carbonic acid, is chocolate-brown; that with hydrogen is brighter. The addition of water alters the colour but little, even when an equal volume is added. If the ordinary mixture of blood with water be agitated with air, it becomes bright and opake; with a saline solution it becomes bright and turbid. If the blood be strongly exhausted under the air-pump, and then treated with a salt, it becomes brighter than when it has not been exhausted, because the carbonic acid which caused the blackening is removed. If dark blood, in which but few and very small corpuscles can be perceived, be agitated with air, it becomes transparent. Addition of a salt does not change it. The action of different salts is tolerably uniform at first. Sulphate of soda, muriate of ammonia and chloride of sodium make the blood uniformly scarlet-red; but after a time, especially with chloride of sodium, the colour becomes gradually darker. Carbonic acid renders this blood still darker.—*Journ. für Prakt. Chem.*, xxxviii, p. 273.

Curious Oxidation of a Lead-pipe.
By THORNTON J. HERAPATH, Esq.

An extraordinary instance of the oxidation of a lead-pipe occurred some little time ago at our Philosophical Institution. Upon taking up the lead-pipe of the pump in the laboratory, it was found to have been converted into a brittle, dark red substance, with occasional indentations going from without inwards. In some places the action had gone to a greater extent, so as to produce large holes in the pipe.

Upon examining some pieces which had been chipped off, they appeared to be composed of consecutive layers of this dark red substance, but between each layer were minute crystals of carbonate of lead.

Upon subjecting some of the pieces to analysis, 100 grs. were found to contain of—

Carbonate of lead	12·884
Protoxide of lead, or litharge	86·594
Water and loss	0·522

100·000 grs.

The only cause to be conceived, to which this extraordinary oxidation could be assigned, is that the pipe followed the course of a drain, which was occasionally used for the conveyance of the refuse of the troughs of some galvanic batteries, the sulphuric and nitric acids of which may have so acted on the lead as to occasion the oxidation of it.

Old Park, Bristol, October 17, 1846.

On the Cyanurate of the Oxide of Amyle. By A. SCHLIEPER.

A short time ago Professor Liebig drew attention to a beautiful crystalline compound which he had obtained by the action of cyanic acid upon fusel oil; at his request I have submitted this body to a more minute examination, and have obtained the following results:—

To prepare this body, perfectly dry cyanuric acid is heated in a small retort, and the vapours of cyanic acid which are formed passed into anhydrous fusel oil. The gas is rapidly absorbed by the fusel oil, with considerable disengagement of heat; after the action has been carried on some time it begins to become thick, and deposits some crystals; and if it be now allowed to cool, the whole liquid congeals to an almost solid paste of crystalline spangles, which form the new compound. To free it from adherent fusel oil and cyamelide, the mass is dissolved in hot water and boiled, constantly renewing the water, until the odour of fusel oil has entirely disappeared; the body then separates on cooling from the hot filtered liquid in crystals. On analysis it yielded—

Carbon.....	48·49	48·75	..	42	=	3150	48·30
Hydrogen.....	8·05	8·12	..	42		525	8·04
Oxygen.....	..	..	..	18		1800	27·57
Nitrogen	..	..	16·36	6		1050	16·09

leading to the formula $C^{42} H^{42} N^6 O^{18} = 2Cy^3 O^3, 3AylO, 9aq$. This compound is therefore cyanurate of amyle, containing only 2 atoms of cyanuric acid to 3 atoms of oxide of amyle; or 2 equivs. of crystallized cyanuric acid have combined with 3 equivs. of the hydrated oxide of amyle. In the perfectly analogous combination with ethyle, 3 equivs. less water enter into the composition, it being expressed by $2Cy^3 O^3, 3AeO, 6aq$.

The cyanurate of amyle, prepared as above described, forms snow-white, very voluminous scaly crystals of the most beautiful mother-of-pearl lustre; it is fatty to the touch, and perfectly void of smell and taste. In its physical properties it has great resemblance to leucine, from which however it differs in being soluble in æther. It is insoluble in cold water, and is not moistened by it, owing to its fatty nature, but is dissolved with tolerable ease by hot water, and the hot saturated solution immediately becomes covered with a beautiful iridescent pellicle; it has no action upon vegetable colours, and is not precipitated by metallic salts. On the cooling of the aqueous solution, it separates in large flakes, which consist of aggregations of very minute needles, which when dried acquire the above-mentioned scaly appearance. It dissolves with tolerable ease in æther and alcohol, and is precipitated from the latter solution by water. Fusel oil is readily obtained from it by alkalies with the assistance of heat; but ammonia, nitric acid, chlorine, bromine and sulphuretted hydrogen have no action upon it. It melts at a gentle heat, and sublimes undecomposed; but the point of fusion and that of decomposition are not far from one another. At 212° it sublimes between two watch-glasses in beautiful shining laminæ; heated more strongly, the mass boils, disengages considerable quantities of fusel

oil, and leaves a white crystalline residue, which dissolved in a cold solution of potash, and was precipitated by acids as a crystalline powder, which gave on analysis, after drying at 212° —

Carbon.....	27.96	6 =	450.0	27.90
Hydrogen	2.46	3	37.5	2.32
Oxygen	..	6	600.0	37.23
Nitrogen	..	3	525.0	32.55

The residue consists therefore of pure cyanuric acid, and the cyanurate of amyle is simply decomposed into its constituents by heat.

Since, according to the investigation of Cahours, the salicylates of methyle and ethyle exhibit such great anomalies, and are in a certain degree entirely removed from the class of the neutral æthers, acting as they do the part of weak acids, the production of the corresponding compound of amyle would have been of great interest. All experiments however made with this view proved fruitless; dry muriatic gas has no other action upon a solution of salicylic acid in fusel oil than the production of chloride of amyle, in whatever way the experiment be modified. The author also attempted to prepare this compound by distilling salicylate of potash with oxylate of amyle; but the distillate consisted merely of unaltered oxylate of amyle mixed with hydrate of phenyle; and on distilling sulphoamylate of lime with salicylic acid, the result was merely a decomposition of the latter into hydrate of phenyle and carbonic acid. It was probable therefore that this compound did not exist in the liquid state, being decomposed by heat. On this supposition, fusel oil was kept boiling for several days with salicylic acid without any change being perceptible; and salicylic acid heated in a sealed tube with fusel oil to 482° , only yielded carbonic acid, hydrate of phenyle and unaltered fusel oil. These experiments seem to prove the non-existence of a salicylate of amyle.—Liebig's *Annalen*, July 1846.

On the Products of Oxidation of the Essential Oil of Fennel by Chromic Acid. By C. W. HEMPEL.

Persoz states that, on treating the essential oil of aniseed, star anise and fennel with a mixture consisting of 6 parts oil, 50 bichromate of potash, 110 sulphuric acid and 400 water, he obtained acetic acid and two new acids, one of which he calls umbellic, and the other badianic acid. At the suggestion of Prof. Liebig I repeated these investigations, in order to ascertain the distinctness of these two acids, or to prove their identity with already known ones. I employed, in forming the above mixture, 40 grms. of oil of fennel. The action was extremely violent, and soon ceased; after cooling the liquid was strained, the residue washed with water, and boiled with a solution of carbonate of potash in a retort, unaltered oil and acetic acid collected in the receiver; the odour of the distillate likewise indicated the presence of camphor. Upon this the liquid in

the retort was separated from the undissolved portion, precipitated with nitric acid, the precipitate well washed, dissolved in boiling alcohol, the solution decolorized with charcoal and filtered hot, when on cooling the acid was deposited in colourless needles. The residue on the filter yielded when heated in a retort a sublimate of camphor, but the quantity obtained was not sufficient for analysis. The acid, after treatment with some æther, gave on combustion with chromate of lead the following results:—

Carbon.....	62·31	62·87	62·98	63·16	16 =	1200	63·15
Hydrogen ..	5·29	5·37	5·41	5·38	8	100	5·26
Oxygen	32·40	31·76	31·61	31·46	6	600	31·59

which leads to the formula $C^{16}H^7O^5 + Aq$.

To determine the atomic weight, the silver salt was employed; it was prepared by dissolving the acid in ammonia, and precipitating with nitrate of silver. The salt consists of white lustrous laminæ, which are fatty to the touch. It yielded on analysis—

Carbon.....	36·74	16 =	1200·0	37·06
Hydrogen	2·81	7	87·5	2·69
Oxygen	18·86	6	600·0	18·86
Silver	41·59	1	1350·0	41·59

From the above it is evident that umbellic acid is identical both with the dragonic acid, according to the formula which Gerhardt assigned to it, and with the anisic acid discovered by Cahours.

I am not able to state anything definite with respect to the existence of badianic acid; what I have found consists in the following:—It is indifferent as regards the result of analysis whether the acid obtained from the oil of fennel has been treated with æther or not; the so-called badianic acid obtained by volatilization of the æther possesses no essentially different properties from those of the umbellic acid. Persoz states, it is true, that the latter is very sparingly soluble in æther, while the former readily dissolves in it; I have however not been able to observe the sparing solubility of the umbellic acid. Moreover, the crystalline form of both acids is the same, only the grouping of the acid crystallized from æther is different, which probably is owing to the solvent. I am therefore inclined to suspect that the badianic acid is not a distinct acid.—Liebig's *Annalen*, July 1846.

On Native Sulphate of Alumina. By THORNTON J. HERAPATH*.

This mineral was sent from Adelaide, in New South Wales, where it is said to be found native in considerable quantity. It consisted of a mass of crystals, which, when examined under the microscope, appeared to be regular four-sided prisms. These crystals dissolved easily in both hot and cold water; the solution had a sweet, astringent taste, and gave an acid reaction with litmus-paper. When the crystals were heated to about 300° F., they became opaque,

* Communicated by the Author.

and afterwards swelled into a light porous mass, which was almost insoluble in cold water, but dissolved, with but a slight residue of earthy matter, in hot water. Heated to redness, they decomposed, leaving a residue of pure alumina.

The mineral contained in 100 grs.—

Water	46·70
Sulphuric acid.	35·63
Alumina	17·09
Oxide of copper	0·04
Earthy matter.	0·50

99·96 grs.

Therefore it would appear to be composed of $\text{Al}^2 \text{O}^3 + 3\text{SO}^3 + 18\text{HO}$, the sulphate of copper and earthy matter being simple impurities.

Prize Questions.

The *Société Hollandaise* has proposed the following prize questions for the year 1848 :—

1. A critical examination of the instruments which are used to measure gas, with the description of a new apparatus which shall indicate the amount of gas consumed with the greatest accuracy.

2. The opinion that the nitrogen contained in the various organs of plants owes its origin to the ammonia which is diffused in the atmosphere is gaining ground every day. This view is opposed to all that is known respecting the nature of the atmosphere and its influence upon the nutrition of vegetables, and not a single argument exists as yet placing it beyond all doubt. The Society requires that the proofs for and against this view be discussed, and that the quantities of nitrogen contained in plants be determined by fresh investigations.

3. What are the inorganic compounds which are met with in the vegetable kingdom? Which are to be considered as accidental, less necessary and less general; and which as requisite and inseparable from vegetable life?

4. Accurate analyses of the substance of the brain of persons of different ages; and a comparison of the composition of the brain, spinal marrow, and of the nerves of the same individual, as complete as possible.

5. What is the nature of that gaseous odoriferous substance called ozone? What conditions are absolutely requisite to its formation? What is its composition? With what substances does it combine; and in how far can a knowledge of it serve to elucidate several other unexplained phænomena of chemistry?

6. A comparison of the physical, chemical, and for agriculture important properties of guano with those of the most ordinary manures, in order to decide whether the guano possess a stronger manuring power than those, and what is the cause of it. It is desired that the kinds of guano be properly distinguished, and that it

be shown how they should be applied to various soils in the cultivation of the useful plants.

The prize for the solution of any one of these questions is a golden medal of the value of 150 florins, and moreover a present of 150 gulden if the answer is considered worthy. The answers may be written in Dutch, French, English, Italian, Latin or German, and must be provided with mottos in the usual way. They should be forwarded *before* the 1st of January 1848, addressed to "J. G. S. Van Breda, Secrétaire Perpétuelle de la Société, Harlem."

ANALYTICAL CHEMISTRY.

On the Action of Protochloride of Tin and of Metallic Tin upon Sulphurous Acid. By H. WACKENRODER.

THE method described by Pelletier, sen., and subsequently by Girardin, Fordos and Gelis, for detecting small quantities of sulphurous acid by means of protochloride of tin, and which has quite recently been strongly recommended by Heintz in a modified form*, appeared to me worthy of attention; since, with the exception of sulphuretted hydrogen, there is no other ready and sufficiently sensitive reagent for sulphurous acid in all those cases in which there is at the same time a large amount of muriatic acid present, or where the other reagents for sulphurous acid cannot be employed. This applies especially to the examination of muriatic acid for sulphurous acid, which at present occurs very frequently in the muriatic acid of commerce.

Sulphuretted hydrogen indicates, it is true, extremely minute quantities of sulphurous acid in the muriatic acid by the production of a white turbidness; but the reduction of the sulphur may also be caused by other substances, as for instance by chlorine and perchloride of iron, and likewise in a slight degree by the oxygen of the air, so that other tests must be employed to decide with certainty as to the presence of sulphurous acid. Moreover, sulphuretted hydrogen produces with sulphurous acid a new acid of sulphur, which I shall describe in a future paper under the name of pentathionic acid. This new acid, which is represented by the formula S^5O^5 , is not decomposed by sulphuretted hydrogen; and it is precisely its production which renders the purification of the crude muriatic acid, contaminated with arsenic and sulphurous acid, far more difficult than it apparently is.

It was immediately evident however that the mode proposed by M. Heintz for producing the reaction could not ensure any great accuracy. The muriatic acid, to which protochloride of tin has been added, and the whole heated, when it does not yield the yellow precipitate of persulphuret of tin, is to be merely treated with sul-

* Chem. Gaz., vol. iii. p. 499.

phate of copper for the production of sulphuret of copper. But taking into consideration the reactions of sulphuretted hydrogen towards metallic oxides, it is evident that, as recently-precipitated sulphuret of tin is very readily soluble in strong muriatic acid, no yellow precipitate can be produced when a tolerable excess of muriatic acid is present, even when the liquid is concentrated and heated. As the sulphuret of copper is less easily dissolved by strong muriatic acid than the persulphuret of tin, the sulphate of copper is capable of demonstrating the presence of the sulphuretted hydrogen produced, where neither persulphuret of tin, and much less protosulphuret, can be formed in acid liquids; however, the sulphuret of copper is also not wholly insoluble in concentrated muriatic acid.

Now it is readily seen that in this reaction every thing depends on the production of the sulphuretted hydrogen. When this is formed in large quantity, persulphuret of tin may be produced; but in every case, and even when only present in the most minute quantity, it will gradually escape from the acid liquid, and then, although not perceptible to the smell on account of the muriatic acid vapours, may readily be detected in another manner. It is upon this that is based the modification which I have made in the process recommended by Heintz.

The muriatic acid to be tested for sulphurous acid is simply treated with a tolerable quantity of the ordinary protochloride of tin in a test-glass. When other liquids are to be examined which do not contain any free muriatic acid, they must be previously mixed with a tolerable quantity of pure muriatic acid. In examining hydrated sulphuric acid, a couple of drops of water or muriatic acid should be added, in order that the liquid may not thicken. Immediately on the addition of protochloride of tin, the glass is covered with a plate of glass, under which is placed a piece of thick white blotting-paper, which has been moistened with a strong solution of acetate of lead. According to the quantity of the sulphuretted hydrogen disengaged from the sulphurous acid does the lead-paper become more quickly, and in a greater or less degree, black. Extremely minute traces of sulphurous acid require half an hour or more to produce a slight blackening or browning of the lead-paper, which is best perceived by removing the glass plate with the paper, and holding it to the light. When the muriatic acid fumes strongly, a considerable quantity of chloride of lead is formed at the same time on the paper; it is therefore advisable to dilute the acid with some water, when the small quantity of chloride of lead formed does not interfere with the reaction. Sulphate of copper does not answer so well as acetate of lead.

This test is as simple as it is accurate and sensitive; it is far more evident than the turbidness produced by sulphuretted hydrogen and sulphurous acid when mixed with muriatic acid. It is decidedly preferable to this latter test, as it proves the presence of the sulphur in the sulphurous acid. However, pentathionic acid likewise disengages sulphuretted hydrogen under the same circumstances; and

consequently all the other acids of sulphur, with the exception of sulphuric, will do the same.

Various views may be entertained respecting the production of the sulphuretted hydrogen from the sulphurous acid by protochloride of tin, especially in the presence of an excess of strong muriatic acid. Heintz's opinion, that 2SO^2 are decomposed by 6Sn Cl^2 to form SnS^2 , 2SnO^2 and 3SnCl^4 must be so far corrected that only SnS^2 and 5SnCl^4 can be formed in an acid liquid. It appears to me far more simple and probable to assume that 1 atom SO^2 and 1 atom SnCl^2 are mutually decomposed, forming SnS ; while the O^2 and Cl^2 are transferred to the excess of SnCl^2 , and so produce 3SnCl^4 . But since the liquid contains an excess of strong muriatic acid, the SnS is again converted into SnCl^2 and H^2S , which either wholly escapes from the liquid, or depending upon its quantity, may produce the proto- or persulphuret of tin, or merely persulphuret of copper in the acid liquid.

It is quite evident therefore, from what has been above stated, that metallic tin may be employed instead of the protochloride for the detection of sulphurous acid, when at the same time a sufficient quantity of strong muriatic acid is added to the liquids. Indeed, pure tin foil appears to indicate still smaller traces of sulphurous acid than the protochloride; it is however necessary each time to ascertain whether the tin foil be pure from sulphur. A moderately dilute muriatic acid mixed with a very little sulphurous acid disengages sulphuretted hydrogen with tin foil, even at the ordinary temperature, without any bubbles of gas appearing near the metal. The crude fuming muriatic acid, which generally contains much sulphurous acid, dissolves the tin foil at the ordinary temperature of the air, with a considerable disengagement of gas and diffusion of an extremely fœtid odour, which has frequently been erroneously considered to be arseniuretted hydrogen; but this is probably contained in the escaping gases after the sulphurous acid has been entirely destroyed, which does not take place so easily. No separation of persulphuret of tin occurs, at least as long as there is a large excess of acid present.

The best method of testing crude and rectified sulphuric acid for sulphurous acid, consists in mixing it with protochloride of tin and a few drops of water, with the application of the lead-paper above described. As a very excellent and pure genuine monohydrated sulphuric acid produces upon, or rather in, the lead-paper a stain, which appears blackish by transmitted light, I am induced to think that traces of sulphurous acid occur in most kinds of crude sulphuric acid. Good rectified sulphuric acid leaves the lead-paper, under similar circumstances, perfectly colourless by transmitted light.

I have still to observe, that both kinds of concentrated sulphuric acid, the crude and the rectified, disengage not a trace of sulphuretted hydrogen from pure chloride of sodium; but that a concentrated solution of sublimed sal-ammoniac mixed with the sulphuric acid sometimes indicates by the lead-paper the liberation of a trace of sulphuretted hydrogen.—*Pharm. Cent. Blatt.*, Sept. 5, 1846.

*On the Detection of Pus in Blood and other Fluids.**By* DR. HELLER.

If the quantity of pus contained in the blood is small, the blood does not exhibit anything remarkable; if a larger quantity is present, the fibrine becomes diminished; and when in very considerable quantity, it disappears almost entirely. If no fibrine is present, on setting the blood aside, the blood-corpuscles are deposited, the pus-cells forming a dirty-white layer above them. This circumstance may therefore be applied to the detection of small quantities of pus in blood. Thus the blood to be examined is allowed to coagulate, the serum is removed, the upper layer of the cruor, having been taken off with a knife, is agitated with water and strained through linen. The liquid is set aside in a narrow glass cylinder for several hours. Most of the blood-corpuscles are dissolved if enough water has been added, whilst the sediment is composed of pus-cells with some chyle-corpuscles. The water is then poured off, and the sediment placed with a little water in a narrow glass cylinder; this is best one-third of an inch in diameter, and the pus-cells are again allowed to subside until the water appears clear. The deposit is then placed under the microscope, and the pus-cells can be distinctly perceived. The chyle-corpuscles are readily distinguishable, as they never exhibit nuclei and are always smaller than the pus-corpuscles. In this manner all the pus in a pound of blood may be collected into a drop, and we may ascertain with certainty the presence or absence of pus in blood. If the blood is quite recently drawn, the fibrine may be removed by heating, and the serum then allowed to subside, by which means we more easily attain our object.—*Archiv für Phys. und Pathol. Chem.*, 1845, p. 303.

On the Quantitative Determination of Urea in Urine altered by Disease, with additional Remarks on its Estimation in Healthy Urine. *By* W. HEINTZ.

Last year the author published a method* for determining urea, in which it was decomposed by sulphuric acid, and its amount calculated from the quantity of ammonia and carbonic acid, products of its decomposition, obtained. In the experiments instituted by the author for this purpose, there were two cases in which the amount of carbonic acid was greater than it should have been in proportion to the urea in the urine. The author found this difference to arise from the recent morning urine, when warmed with sulphuric acid, sometimes evolving a small quantity of carbonic acid. Two more experiments were therefore made, previously to which the urine was boiled once to expel the carbonic acid. They yielded—

	I.	II.
Urea, calculated from the carbonic acid	22.24	12.92
Urea, calculated from the platinum	22.60	12.83

* *Chem. Gaz.*, vol. iv. p. 17.

The agreement of these analyses is such as to leave no doubt that the difference arose from the carbonic acid contained in the urine.

Another objection to the author's method may be made from Scherer's having found nitrogen in the extractives of the urine; but since 100 parts of the extractives contain 3.91 of nitrogen, the amount of the extractive matter in the urine compared with the urea is much too small to give rise to an error of any importance; in four experiments the error amounted to 0.18, 0.16, 0.11 and 0.15 per 1000. The author formerly considered this error partly to arise from a portion of the uric acid going down with the oxide of lead used to separate the extractive matter; but since Scherer completely separated the uric acid by alcohol, the formation of the ammonia must be ascribed to the extractive alone. In his former experiments the author precipitated the extractive matter with basic acetate of lead, and decomposed the precipitate with sulphuretted hydrogen. As, according to Scherer, the extractive is changed by the muriatic acid, which is formed simultaneously with the precipitate of chloride of lead, he performed the experiment exactly according to Scherer's method. 100 grms. of morning urine were precipitated with basic acetate of lead, the precipitate washed, and immediately heated with muriatic acid upon the filter. The fluid thus obtained was diluted with a mixture of equal weights of alcohol and water; to precipitate the chloride of lead completely, the filtrate was evaporated, and the ammonia contained in it was estimated in the ordinary way. The ammonia thus found amounted in one case to 0.18, in the other to 0.16 per 1000. But since uric acid was still found in this extractive, the error, after allowing for this, would become still less. That diabetic urine, the only anomalous constituent of which is sugar, might be examined according to the method given by the author, he has previously shown; the next point is, how far his method may be applicable to those cases in which other abnormal constituents occur in the urine.

Albumen in Urine.—The author mixed urine partly with blood-serum, partly with egg-albumen; precipitated a specimen of it with alcohol, and satisfied himself that chloride of platinum detected mere traces of potash and ammonia in the filtrate. Egg-albumen or blood-serum was then treated, according to the method described, with sulphuric acid; and in this way a considerable quantity of ammonia was obtained. Hence it follows, that if it is required to examine urine according to the author's method, the albumen must previously be separated completely. Albumen is not always perfectly precipitated by boiling, even from acid urine. Neither should nitric acid be used for this purpose, since in the subsequent treatment with sulphuric acid, nitrous acid would be formed, which, as is known, decomposes the urea so as to liberate part of the nitrogen in the gaseous state. Even with alcohol a considerable amount of albumen remained unprecipitated in many cases; however, this appeared to be prevented by treating the urine with a few drops of sulphuric acid before adding the alcohol. 7.512 grms. of the serum of the blood, which, after separating the albumen by sulphuric acid and

alcohol, was evaporated with concentrated sulphuric acid, and heated to 374° F., yielded a precipitate with chloride of platinum, which, after heating to redness and washing with muriatic acid, left 0.0533 grm. of platinum. In a second experiment, 6.3456 grms. of serum gave only 0.0055 grm. of platinum; in a third, 0.0007 grm. of platinum was obtained from 7.1953 grms. of blood-serum which had not been heated with sulphuric acid; whilst 5.7017 grms. of the same serum, when heated with sulphuric acid, gave 0.0232 grm. of platinum. Some ammonia was therefore formed by the action of the sulphuric acid. Moreover it is very difficult to wash with alcohol the albumen precipitated by alcohol, since the fluid runs through but very slowly; and, as Marchand has shown, it is impossible to extract all the urea from the coagulated albumen.

The author next examined the application of the bichloride of mercury as a means of separation. The precipitate formed in albuminous solutions by bichloride of mercury is very voluminous, and in concentrated solutions gelatinous. However, when heated it contracts, and may then be readily filtered and washed. To remove the excess of the bichloride, the author at first treated the liquid before filtering with sulphuretted hydrogen; but a little sulphuret of mercury then always passed through the filter, whence it follows that some of the coagulated albumen must have been redissolved. The precipitate obtained by boiling with bichloride of mercury was then first separated by filtration, and the excess of the bichloride was precipitated from the filtrate by sulphuretted hydrogen, by which method the filtration and washing is very readily effected. 5.7780 grms. of blood-serum, thus treated and heated with sulphuric acid, &c., yielded 0.0017 grm. of platinum; whilst 7.5467 grms. of the blood-serum, which had not been treated with sulphuric acid, gave 0.0010 grm. of platinum; hence 0.29 and 0.13 per 1000. The difference, 0.16 platinum per 1000, would cause an error of 0.05 per 1000 of urea. In another experiment 1000 parts of serum gave 0.75 and 0.47 part of platinum. The difference, 0.28, would correspond to 0.09 per 1000 urea. Thus these errors are so small as not to be capable of exerting any essential influence on the estimation of the urea; and hence the author's method is perfectly susceptible of application to the estimation of the urea in albuminous urine. To estimate then the urea in albuminous urine, a carefully weighed portion of the urine is treated with bichloride of mercury and boiled in a capacious dish. The liquid is then filtered, the precipitate slightly broken up and washed with water. When this is perfectly effected, a slow current of sulphuretted hydrogen is passed through the filtrate, and the liquid is filtered from the sulphuret of mercury formed. The separation of the mercury may also be omitted, if care be taken to guard against the vapours of mercury which escape on heating it with sulphuric acid. The filtrate is evaporated with the addition of sulphuric acid, until the sign of the perfect decomposition of the urea pointed out by Ragsky occurs, viz. the complete cessation of the evolution of bubbles. The fluid thus obtained is then treated as

previously described *. Another weighed portion of the urine is also precipitated with bichloride of mercury, the precipitate washed with alcohol, and the filtrate treated with bichloride of platinum and æther. The platinum obtained from the precipitate enables us to calculate the amount of potash and ammonia in the urine.

Blood in Urine.—As all the constituents of the blood are occasionally found in the urine, it remained to be proved that the above method was also here applicable to the estimation of the urea. For this purpose blood was treated in the same manner as the serum above-described. 1000 parts of the blood of the herbivora, treated as above with sulphuric acid, gave 1·67 part of platinum, whilst, when not treated with the acid, they gave 1·05 platinum. The difference, 0·55, would correspond to 0·17 urea per 1000. As the amount of the components of the blood occurring in the urine is always small, the error caused by it must be extremely minute.

The author also shows that his process is applicable to the estimation of the urea in urine containing milk as well as bile. In the latter case, should the quantity of urea amount to one-ninth of that of the urine, which could hardly occur, the error would only be 0·16 per 1000.—Poggendorff's *Annalen*, lxxviii. s. 393.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Gun-Cotton.

GREAT interest has of late been excited by the announcement of a substitute for gunpowder. No sooner was the name of *gun-cotton* made public than it was generally surmised by chemists that it must be some preparation identical with, or closely resembling Xyloidine, a substance discovered by Braconnot in 1833, and subsequently described more fully by Pelouze in the 'Comptes Rendus' for October 15th, 1838. In this paper, after describing the preparation and various properties of this body, M. Pelouze states "that it is very combustible, takes fire at a temperature of 180° Cent. (356° F.), and burns with considerable vivacity, leaving scarcely any residue. This property has led me to an experiment which I think susceptible of some applications, especially in artillery. On immersing paper in nitric acid of 1·5 spec. grav. until thoroughly penetrated by it, which occupies scarcely 2 or 3 minutes, and well washing it with water, a kind of parchment is obtained, which is impermeable to moisture and of extreme combustibility. The same happens with linen and cotton."

This substance, therefore, if not the gun-cotton of Prof. Schönbein, most closely resembles it in many of its properties; but, although its application is here suggested, we are not aware that it was ever

* Chem. Gaz., vol. iv. p. 18.

introduced before being brought before the public by Prof. Schönbein, to whom justly belongs the credit of applying it to useful purposes.

Since the announcement of Prof. Schönbein's experiments with this explosive substance, several letters have appeared in the public prints, which, as they describe more minutely the preparation of the gun-cotton, we make no reserve in transferring to our pages. The first is by Dr. Otto of Brunswick, who published the following statement in the '*Hanoverian Gazette*,' whence it was copied into the '*Times*':—

"Entirely independent of Schönbein and Böttger, but relying on an observation of Pelouze, I have succeeded in producing an exploding cotton, which, after a series of experiments, seems quite suited to supply the place of gunpowder. In order to bring the results of important discoveries as speedily as possible to the highest state of perfection, it seems to me necessary to lay them immediately before the public, in order that many persons may turn their attention to the subject. I scorn therefore to sell or take out a patent for my very interesting discovery*, the consequences of which are not easy to be foreseen; and I now publish it for the general good of the public.

"In the preparation of the exploding cotton, common well-cleaned cotton is dipped for about half a minute in highly concentrated nitric acid (the acid which I use being made by the distillation of 10 parts of dried saltpetre and 6 of oil of vitriol), and then instantly placed in water, which must be often renewed, in order to free the cotton from the acid with which it is impregnated. Care must then be taken that all the knotty particles of the cotton are properly disentangled, and that it is thoroughly dried. After this the explosive preparation is ready for use. Its effects create astonishment in all who witness them, and the smallest portion explodes when struck on an anvil with a hammer, like fulminating powder; when kindled with a glowing body it takes fire just like gunpowder; and when used in a gun, its operation, though in a far greater proportion to its weight, is precisely the same as that of gunpowder. This gun-cotton is employed exactly in the same way as gunpowder; a piece of it is rammed down the barrel, then a bit of wadding, and after that a ball; a copper cap ignites and explodes the cotton. Without a single exception, all who have witnessed my experiments have been most completely satisfied, but no one has mentioned the matter."

"Brunswick, Oct. 5."

This letter soon led to the following, addressed to the Editor of the '*Times*':—

"SIR,—From reading the observations on gun-cotton which have recently appeared in the '*Times*' newspaper, I was induced to make some experiments upon the subject, and in particular to try the process recommended by Dr. Otto, of immersing cotton for half a

* If the very interesting discovery had not been made long before, would Dr. Otto have been the first to make it?

minute in strong nitric acid, and merely washing and drying it. This process did not succeed, undoubtedly from my not having employed an acid sufficiently strong. I find however that a highly explosive cotton may be prepared with the ordinary nitric acid of commerce, by previously mixing it with about one-third of its volume of sulphuric acid (oil of vitriol). The cotton, when immersed in this mixture, quickly becomes whiter, more opaque, and loses its elasticity. After having assumed this appearance, which it does in the course of a few minutes, it is to be taken out and well-washed in water, so as to remove the slightest trace of acid. It may then be squeezed in a linen cloth, dried and carded. Thus prepared, the cotton differs very little in appearance from ordinary cotton, except that it is more harsh to the feel. On the application of an ignited body, it explodes without leaving the slightest residue; and my friend Dr. Leeson, who repeated, with some cotton prepared in the above manner, several of Dr. Schönbein's experiments, could not perceive the least difference between its effects and those he had witnessed at Southampton. It readily exploded when struck by a hammer, and could be fired over gunpowder without igniting the latter. There can therefore be no doubt but that the two substances are chemically identical; whether prepared in the same manner I am of course ignorant, as Dr. Schönbein has not as yet published his process. If not, he will have the advantage of including the above process in his specification; and I heartily trust that he may reap the full reward of his discovery, to which he is certainly entitled, as having been the first to draw public attention to the properties of this curious body; it appearing to me a matter of very little consequence (as regards his rights) whether his process and those subsequently proposed by others are precisely identical. The process I have recommended is of course only a modification of Dr. Otto's; it has the advantage however of being much cheaper and more easily managed. The strong acid used by him is not only very expensive, but is rarely to be met with, while sulphuric acid and common nitric acid are very cheap, and may be procured anywhere. So simple is the process, that sufficient cotton may be prepared to exhibit all its characteristic properties in the course of 10 minutes; and if this substance ever comes into practical use, the sportsman might prepare his stock of powder just before he started.

"Your obedient Servant,

"THOS. TAYLOR."

"9 New Bridge Street, Blackfriars, Oct. 17."

In a subsequent letter Mr. Thomas Taylor somewhat modifies his previous statements and process. He recommends "mixing in any convenient glass vessel $1\frac{1}{2}$ ounce by measure of nitric acid (sp. gr. 1.45 to 1.50) with an equal quantity of sulphuric acid (sp. gr. 1.80). When the mixture has cooled, place 100 grains of fine cotton wool in a Wedgewood mortar, pour the acid over it, and with a glass rod imbue the cotton as quickly as possible with the acid. As soon as the cotton is completely saturated, pour off the acid, and with the aid of a pestle quickly squeeze out as much of

the acid from the cotton as is possible. Throw the mass into a basinful of water, and thoroughly wash it, either in successive portions of water, or underneath a tap, until the cotton has not the slightest acid taste. Finally, squeeze it in a linen cloth, and dry it in a water-bath. By employing a large relative proportion of the acids to the cotton, or by using stronger nitric acid, a still more highly explosive compound may be produced; but acid of the strength and in the proportions I have given affords a very useful article at a moderate cost. Nitric acid of the sp. gr. of 1.50 answers much better than that of 1.45; it being a curious fact that the texture of the cotton is much less acted upon by the stronger acid. If the nitric acid has only the sp. gr. of 1.36, the cotton is often converted into a gelatinous mass, and I have no doubt but that in the majority of cases where persons have failed in repeating my process, the failure is owing to their nitric acid being too weak. By the ordinary acid of commerce I meant that of the 'London Pharmacopœia,' which should be of the sp. gr. 1.50, but is seldom more than 1.45. When the very best cotton is required, it will be found advantageous to remove all adhering grease by first washing the cotton in a weak alkaline solution, and thoroughly drying it before it is immersed in the acid. Being unwilling to detract in any way from the value of any other person's process without sufficient trial, I stated in my first communication that my process could only be regarded as a modification of that of Dr. Otto's; it is however something more, for I have carefully repeated Dr. Otto's process, using acid of the sp. gr. 1.512; and I may now venture to assert, that although a powerfully explosive cotton is produced, it is much inferior in strength to that made with the addition of sulphuric acid. The cotton when well-prepared should be perfectly white, and its microscopic structure quite unaltered.

In conclusion, I would observe that the explosive cotton of Schönbein, Otto and myself is an extension of the fact, long known to chemists, that various organic bodies, as paper, flax, cotton, &c., after being dipped into strong nitric acid, acquire the property of burning with the greatest rapidity when ignited.

Your obliged servant,

THOMAS TAYLOR.

9 New Bridge-street, Blackfriars, Oct. 26.

Mr. T. Taylor acknowledges that it is merely the extension of a fact long known. He omits however to mention to whom the credit of the discovery of this body is due, the very application of which, as the reader will see from the paragraph quoted from Pelouze's paper, is suggested as far back as 1838.

From the numerous experiments made with this substance, it promises to be a most valuable substitute for gunpowder, especially for mining purposes, as will be seen from the following account of some experiments made by Richard Taylor, Esq. of Pennear, and Professor Schönbein, given at the last annual meeting of the Royal Geological Society of Cornwall:—

"After briefly describing the characteristics of the cotton, Mr. Taylor proceeded to relate the particulars of the experiments

made in Cornwall. The first place where it was tried was in a granite quarry at Spargo, near Penryn, where the professor and himself were accompanied by Mr. Robert Were Fox, Mr. Alfred Fox, Mr. Barclay Fox, and several other gentlemen, besides Mr. Hoskin the owner of the quarry, and some other people of that class. The surprise and incredulity of the workmen on that occasion were very great. When he (Mr. Taylor) charged a hole with cotton, they thought he was doing a very absurd thing, and one of them offered to sit on the hole for a pint of beer. Two holes were selected by the quarryman, of which he had the choice of one, which he charged with a proper quantity of gunpowder. The other hole was then charged with a quarter part of that weight of cotton. The hole charged with powder was fired, and produced its effect most completely. The other hole was then fired, and to the astonishment of the workmen, tore the rock into a number of fragments; it did more than was required, the charge being rather too great. They then proceeded to two very strong holes, in a dense part of the rock, requiring a very strong charge of gunpowder. The charge for one hole was $13\frac{1}{2}$ oz. of powder; for the other hole, 3 oz. of cotton. Both holes were fired, and did their work well—that charged with cotton, to the complete satisfaction of all present. They then made experiments with smaller proportions of cotton; and in one instance, a charge of cotton equal to only one-sixth of the charge of powder, did its work; though he did not rely much on this experiment, because it was probable the workmen had overrated their charge of powder.

“Some other experiments were tried, with the use of sand and wedges; and he might say that throughout the whole, they succeeded uniformly where they had a charge of cotton equal to one-fourth part of a charge of gunpowder. He was next anxious that experiments should be tried with regard to the effect of the explosion of cotton on the air of a mine. For this experiment he selected the iron mine at Restormel, because it was extremely easy of access, and the Professor might enter it without fatigue or difficulty; next, because it was very hard ground; and lastly, because the adit level is driven a considerable distance into the hill, while the end of the level is very close, presenting great difficulty to the escape of smoke. The experiment was tried at the end of the adit level—about 600 or 700 fathoms from the entrance. They fired two holes—one with one-fourth part, and the other with one-sixth part of the weight of gunpowder that would have been requisite. Both charges tore the ground to the complete satisfaction of the miners. The miners stated that if they had fired two such holes with gunpowder, they could not have gone into the place again for three quarters of an hour. On this occasion the whole party of miners went in instantly with two captains, the Professor, and himself. They perceived no inconvenience whatever, beyond a little from the safety-fuze, which was not such as to incommode the men. They then tried an experiment, which, it was supposed by the miners, would upset all former conclusions as to the strength of the cotton. A hole had been bored to a great depth, in a very hard part of the rock, which they asked to have

blasted with cotton. They said their charge of powder would be 1lb. The hole was charged with $\frac{1}{4}$ lb of cotton. It did not tear the ground. The miners, however, said that that was no failure of the cotton; for $1\frac{1}{2}$ lb of powder would not have torn the ground. The hole was charged with 1lb. of powder, and no effect was produced; and one of the captains said if they fired away all the powder that Wellington burnt in the Peninsula, it would not blast the hole—it was as strong as a cannon. He had since found that the men had been working there ever since, and had not succeeded in so far freeing the ground as to enable them to blast with powder—the ground was so hard that it blew out the tamping.

“Mr. Taylor next observed that the mode of charging with cotton was precisely the same as with powder; and it possessed the advantage of being compressible, in the swabbing-stick, into a smaller space than powder. In answer to the Rev. J. Punnett, Mr. Taylor said that Professor Schönbein had informed him that the cotton was not easily inflammable by friction. He believed there was no danger of its being ignited by such friction as it would be subject to in mining uses. Of course, such friction as would produce a heat of 400 degrees, at which point it was inflammable, might ignite it. It was not easily inflammable by concussion; and the effect of concussion was singular. If, for instance, the cotton was struck on an anvil with a hammer, the portion of cotton immediately under the blow was ignited, throwing the surrounding portions off in all directions without igniting them. Mr. Taylor next related the particulars of some very successful experiments on the use of the cotton in rifles and pistols. He had himself imbedded a bullet in a plank at 102 yards, at Wheal Friendship; and brought down pheasants and partridges with one-fourth the weight of an ordinary charge of powder. In reply to a question from Mr. D. P. Le Grice, Mr. Taylor said that, weight for weight, the cotton would probably cost more than gunpowder; but then, with a quarter part of the weight of powder, equal power was obtained. After remarking on the quality of the gun-cotton—that it is uninjured by damp, or even by immersion in water, and on its freedom from danger in the course of manufacture, Mr. Taylor exhibited a few experiments with bits of the cotton, showing its inflammability at a much less heat than required by gunpowder—its entire freedom from smell, and the almost entire absence of smoke or residuum. The cotton which Mr. Taylor had was of *second* quality, and explosion was accompanied with a slight smoke, and a deposit of a few brownish particles, like a light sprinkling of snuff.”

Preparation of a Substitute for Horn. By M. ROCHON.

In many of the arts, more especially where steel instruments are manufactured, glass windows are of great inconvenience, owing to the frequent breakage by fragments of steel. The substitution of horn is attended with some inconvenience, principally on account of its want of transparency. A substitute is proposed to be made of very light cloth or wire gauze composed of fine brass wire, which is

to be immersed repeatedly into a solution of isinglass until all the meshes are filled and a sufficient thickness acquired, after which it is covered with a coat of copal or other varnish to protect it from the weather.—*Voigt. Mag. de Naturk.*, Feb. 1846; and *Silliman's Journal*, Sept. 1846.

PATENT.

Patent granted to Robert Lewis Jones, for an improved Preparation of Charcoal.

THE first part of this invention consists in using currents of air to separate the fine from the coarse particles of charcoal or charred peat, when grinding the same; which fine particles may be employed instead of vegetable black, drop black and lamp black, and also as a substitute for, or combined with black lead, in the preparation of mixtures for lubricating axle-trees and machinery; the coarser particles may be used by iron-founders and others. This invention consists, secondly, in separating the fine from the coarse particles of ground charcoal or charred peat by currents of air, after the same has been ground in the usual manner.

The charcoal or charred peat may be ground in any convenient close mill, but the patentee prefers one of the kind employed in grinding charcoal for the use of iron-founders; and he applies a cover thereto, containing holes for the entrance of the air, and furnished with valves to regulate the supply. From the top of the mill a pipe extends to a rotary fan or other exhausting apparatus, which is connected by another pipe with a long chamber, so constructed that the finer particles may be deposited therein and the air pass away. The chamber is 30 feet long, 10 feet high and 10 feet wide; the top, one end and one side are composed of calico, stretched on light wooden framing, and the other side and end are formed by a wall. The action of grinding will cause the finer particles to rise in the mill, and they will be carried off by the currents of air into the long chamber, where they will be deposited on the floor, or in pockets descending from the floor or other part; and the powder will be of different degrees of fineness, according to the distance from the entrance of the chamber to the place where it is deposited. Although the patentee prefers the apparatus and means above-described, for grinding and producing currents of air, he does not confine himself thereto.

When the charcoal or charred peat has been ground in the ordinary manner, without the employment of currents of air to separate the fine from the coarse portions, the powder is introduced into a covered cylinder, or other convenient vessel, provided with a stirrer, and connected with an exhausting apparatus (similar to the mill above-described), by which the fine particles are caused to proceed to the long chamber wherein they are to be deposited, the coarse particles remaining in the cylinder.—Sealed March 5, 1846.

THE CHEMICAL GAZETTE.

No. XCVIII.—November 16, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Chemical Properties of Ruthenium and some of its Compounds. By Dr. C. CLAUS.

RUTHENIUM occurs in the residues of the Russian and also of the American platinum ores, but only to the small extent of $1-1\frac{1}{2}$ per cent. It is a constituent of osmium-iridium; the varieties of this mineral analysed by me contained, besides osmium and iridium, 3-6 per cent. ruthenium, 10 per cent. platinum, $1\frac{1}{2}-2$ per cent. rhodium, with traces of copper, iron and palladium. The mineral described by Herman under the name of irite contains 3 per cent. Ru along with Rh, Pt, Os, Ir, FeO, Cr^2O^3 , Al^2O^3 , SiO^3 and IrO^2 . The ruthenium does not occur in that portion of the platinum ore which is soluble in *aqua regia*; it was discovered in the platinum residues, because these always contain osmium-iridium.

The following is the method which I adopt at present for its preparation:—Osmium-iridium is powdered as finely as possible in a cast iron mortar; the particles of iron removed from the mortar are extracted with muriatic acid, and the powder mixed with chloride of sodium treated at a faint red heat with moist chlorine gas. The decomposed mass is extracted with cold water, and a few drops of ammonia added to the concentrated brownish-red, almost opaque solution, which is then heated in a porcelain dish. A voluminous blackish-brown precipitate, consisting of sesquioxide of ruthenium and oxide of osmium, is thrown down. This, after edulcoration, is heated in a retort with a sufficient quantity of nitric acid until the acid has passed over, and the osmium removed as osmic acid. The residue in the retort is removed, ignited with nitre and caustic potash which is free from silica, in a silver crucible, for an hour, and the ignited mass softened and dissolved in cold distilled water. The solution is left to clear for 2 hours in a corked flask, the perfectly transparent, beautiful orange-coloured solution removed with a siphon from the insoluble portion, and the alkaline liquid neutralized with nitric acid; this produces a precipitate of velvety-black sesquioxide of ruthenium, which after edulcoration and drying is reduced in a current of hydrogen. In this way perfectly pure metallic ruthenium is obtained. This mode of separating it from the other platinum metals, with the exception of osmium, is based on the behaviour of the solution of
Chem. Gaz. 1846.

the sesquichloride of ruthenium, which is decomposed by heat into free muriatic acid and sesquioxide. The oxide of osmium is mixed with the oxide of ruthenium, as the solution contains chloride of osmium, which is likewise decomposed. The osmium-iridium is only partially decomposed in the above treatment with chlorine, and must therefore be treated with it three or four times.

Ruthenium thus prepared forms angular pieces, of metallic lustre, which are porous, and very closely resemble iridium. Its specific gravity is very low, viz. 8.6 at 61° F.; but it is highly probable that it is but little inferior in this respect to iridium, for some porous iridium, which was prepared in a similar manner from the blue oxide of iridium IrO_2 , had a specific gravity of 9.3. Ruthenium is very brittle, does not fuse in the flame of the oxyhydrogen blowpipe, and is almost insoluble in acids; *aqua regia* dissolves mere traces of it. After osmium, ruthenium has the greatest affinity for oxygen of all the platinum metals, for it is very readily oxidized on heating to redness. There are four oxides of ruthenium:—

I. *The protoxide*, RuO , is obtained when 1 equiv. RuCl^2 is heated strongly with rather more than 1 equiv. NaO CO^2 in a current of carbonic acid, and then extracted with water. The protoxide is left as a blackish-gray metallic powder, which is insoluble in acids, and is reduced by hydrogen at the ordinary temperature. It is anhydrous, and contains in 100 parts 86.6 ruthenium and 13.4 oxygen. The hydrate is still unknown, and will probably be as difficult to prepare as the hydrate of the protoxide of iron.

II. *Sesquioxide*, Ru^2O^3 . *Anhydrous*.—When the pulverulent metal is exposed to a bright red heat in a platinum crucible over Piclet's glass-blower's lamp, it acquires a black colour, and very quickly absorbs for every 100 parts 18 parts oxygen; subsequently the oxidation slowly proceeds further until the oxide becomes blackish blue, and then contains 23–24 parts oxygen to 100 of ruthenium. This oxide increases still more in weight when exposed to a very long-continued red heat, but it could not be oxidized to RuO^2 .

The *hydrate*, $\text{Ru}^2\text{O}^3 + 3\text{aq}$, is obtained by precipitating the sesquichloride with alkalis. It must be well washed, and nevertheless contains a few per cent. of the alkali. It forms a blackish-brown powder, which dissolves with an orange colour in acids, glows suddenly when heated, and is not perfectly reduced at the ordinary temperature by hydrogen. It is insoluble in alkalis.

III. *Oxide of Ruthenium*, RuO^2 . *Anhydrous*.—On roasting and igniting RuS^2 , a blackish-blue powder, with a greenish play of colours, is obtained, which is insoluble in acids, and contains 30.7 parts oxygen to 100 of metal. It is obtained when $\text{RuO}^2, 2\text{SO}^3$ is exposed to a strong red heat in small grayish particles of metallic lustre, and with a beautiful blue and green iridescence.

The *hydrate*, $\text{RuO}^2 + 2\text{aq}^?$, has not yet been analysed, but it will undoubtedly possess the above composition; it is obtained as a gelatinous yellowish-brown precipitate, when the solution of the double chloride $\text{KCl}^2 + \text{RuCl}^4$ is mixed with NaO CO^2 , and evapo-

rated. It contains much alkali, dissolves with a yellow colour in acids, and these solutions become of a rose-red on evaporation. When heated in a platinum spoon it detonates with a lively incandescence, and is projected in all directions. In the dry state it has the colour of impure oxide of rhodium.

IV. *Ruthenic acid*, RuO_3 , is not yet known in its isolated state. It is most probably a very unstable compound, which is readily decomposed into oxide and oxygen. It occurs as basic ruthenate of potash in the solution of the ruthenium which has been ignited with potash and saltpetre. The composition of the acid was ascertained in the same way as H. Rose analysed the ferrate of potash. For the analysis however a ruthenate of potash was employed, which had been prepared by igniting the metal with potash and chlorate of potash. The salt could not be obtained crystallized, as the solution is readily decomposed. The solution is of a beautiful orange colour, is very astringent to the taste, like tannic acid, and is neutral, if too much potash and nitre has not been used in its preparation; it colours organic substances black, owing to a deposition of reduced oxide. Acids immediately precipitate from it a black oxide, which contains potash if the solution had not been perfectly neutralized with acid; with a slight excess of acid however the precipitated oxide contains some per cents. of acid. When sulphuric acid is used, a metal is obtained on reducing the oxide which contains some sulphuret, and which it is very difficult to decompose at a faint red heat in a current of hydrogen. I analysed the oxide containing acid, especially that precipitated by nitric acid, and obtained results which led me to believe that this oxide was $\text{RuO}_3 + 2\text{aq}$ (I was not then acquainted with the true hydrated oxide); but it is very probable that, on igniting it in a current of carbonic acid in order to determine the water, the sesquioxide is converted by the action of the nitric acid into oxide. At present I consider this black oxide to be a hydrate of the sesquioxide, because it dissolves in muriatic acid, forming sesquichloride*.

Chlorides of Ruthenium.

I. *Protochloride of Ruthenium*, RuCl .—In my former experiments it appeared to me as if ruthenium were little acted upon by chlorine. I subsequently observed however that after very long-continued treatment the metal was converted at a faint red heat into protochloride. When ruthenium is heated to redness in the bulb of a reduction-tube over an Argand lamp, and dry chlorine passed over it, yellow vapours (probably the highest and most volatile chloride) are first disengaged and carried away by the current of gas; the metal seems not to change and to increase in bulk; subsequently some sesquichloride sublimes, and the metal becomes black; after 2 hours it is converted into a black partially crystalline protochloride. It is however not always possible to saturate the ruthenium

* Before I was acquainted with the true oxide and perchloride, I thought that muriatic acid converted the black oxide with reduction into sesquichloride, especially as some chlorine was disengaged in the experiment.

perfectly with chlorine in one operation; it is best to reduce the protochloride formed to a fine powder, and to treat it again with chlorine. In this way a combination is always obtained, yielding on analysis numbers corresponding to the above formula. Water removes a trace of sesquichloride from it; otherwise it is insoluble in it and in acids; a solution of caustic potash has little action upon it even when evaporated with it to dryness.

Soluble Protochloride.—When the solution of the sesquichloride is treated for a long time with sulphuretted hydrogen, a black-brown sulphuret is precipitated, and the liquid acquires the well-known beautiful azure-blue colour. The sulphuretted hydrogen can be removed from this fluid by a current of atmospheric air, and in this way a solution of the blue protochloride with muriatic acid obtained. I regard this blue combination as the protochloride, although I cannot vouch for the correctness of this view; for it is not possible to prepare it in a solid form or as a crystalline double salt, as it is very readily decomposed, and passes into the orange sesquichloride. I therefore attempted to obtain an idea of the composition of this compound by precipitating the solution of the blue protochloride by alkalis; but the oxide thus obtained possessed the composition of sesquioxide Ru^2O^3 . This negative result is no direct proof against my view, for I have observed that, in the decomposition of the lower chlorides of iridium by alkalis, the higher oxide IrO^2 is constantly formed. Ruthenium must behave similarly, as it exhibits a greater affinity for oxygen than that metal. The reasons which have led me to regard the blue compounds as the protochloride are,—1st, HS, in its action upon the perchlorides of the other platinum metals, converts them into lower chlorides; 2nd, the sulphuret which separates on the formation of the blue compound does not contain, as it should, 3 atoms of sulphur to 2 of metal, but 2 and more atoms of sulphur to 1 atom of metal; 3rd, other reducing agents, as zinc, percyanide of mercury, &c., colour the sesquichloride blue; 4th, on heating the evaporated solution of the sesquichloride, it becomes green (a mixture of blue and yellow protochloride), and at some spots blue; but it is not possible to prepare in this manner a pure blue protochloride, because a portion of the salt is converted into a basic compound.

II. *Sesquichloride of Ruthenium*, Ru^2Cl^3 , is obtained by dissolving the sesquioxide, precipitated from the ruthenate of potash, in muriatic acid, and evaporating to dryness. It is deliquescent, has a very astringent non-metallic taste, like tannic acid; and dissolves, leaving behind the yellow basic compound, with a beautiful orange-red colour in water and spirit. When heated it acquires the above-mentioned green and blue colour. One of its most remarkable properties is that its dilute solution is decomposed by heat into free muriatic acid and hydrated sesquioxide. This decomposition takes place likewise at the ordinary temperature in the course of a few days.

Caustic and carbonated alkalis, as well as the tribasic phosphate of soda, immediately produce in the solution of this salt a blackish-

brown precipitate of hydrated sesquioxide, which is not soluble in an excess of the precipitant. Some unprecipitated metal is however left in the solution. Solution of borax at first produces no precipitate, but merely decolorizes the solution, which on the application of heat deposits $\text{Ru}^2\text{O}^3 + 3\text{aq}$. Formiate of soda does not reduce the metal, but only decolorizes the solution; the same happens with oxalic acid. Ferrocyanide of potassium at first decolorizes the solution, which subsequently becomes green. Percyanide of mercury colours the solution blue, with formation of a blue precipitate. Nitrate of silver yields a black precipitate, which subsequently turns white, while the liquid becomes rose-red. Chloride of potassium and chloride of ammonium produce dark brown crystalline precipitates only in very concentrated solutions. Sulphurous acid decolorizes the sesquichloride only after long-continued action. Sulphuretted hydrogen produces the above-mentioned blue reaction, with deposition of sulphuret. Sulphuret of ammonium throws down most of the ruthenium from the solution as a blackish-brown sulphuret, which is not perceptibly soluble in an excess of the precipitant.

III. *Perchloride of Ruthenium*, RuCl^2 .—This compound is not known in the isolated state; it exists however in combination with chloride of potassium. In the double salt described below it has the rose colour of the salts of the perchloride of rhodium (Rh^2Cl^3).

Double Salts.

I. *Sesquichloride of Ruthenium and Potassium*, $2\text{KCl} + \text{Ru}^2\text{Cl}^3$.—From the composition of this salt the atomic weight of ruthenium was ascertained, and found to be identical with that of rhodium. The analyses of the other compounds of ruthenium have fully confirmed this determination. In the crystallized state it is perfectly insoluble in alcohol of 0.865 spec. grav., and possesses in this respect the properties of the double chlorides of all the other platinum metals with potassium and ammonium. When however the salt is in a concentrated solution, alcohol only throws down a portion; when the solution of the salt is mixed with the chloride of any other metal soluble in alcohol, evaporated to dryness, and digested with strong spirit, the salt of ruthenium dissolves in proportion to the quantity of the other soluble chloride. This property is likewise possessed by the sparingly soluble double salts of other platinum metals, among others by the sodiochloride of rhodium. The crystallized sesquichloride of ruthenium and potassium is almost insoluble in a concentrated solution of chloride of ammonium, and I have used this salt in washing the salt of ruthenium, to free it from any admixture of chloride of potassium. This method is far more certain than the employment of spirit, which only removes with difficulty the last traces of that admixture. It is scarcely necessary to observe that the chloride of ammonium must be subsequently extracted with spirit, which however, from the great solubility of the salt, is very readily and quickly effected.

II. *Sesquichloride of Ruthenium and Ammonium*, $2\text{NH}^4\text{Cl} + \text{Ru}^2\text{Cl}^3$, is very easily obtained by mixing the concentrated solution

of the black sesquioxide in muriatic acid with chloride of ammonium, and concentrating by evaporation with the addition of a little nitric acid. The salt cannot be distinguished in form and properties from the potash salt; it leaves, as required by the formula, 32.7 per cent. metal when ignited in a current of hydrogen. Both these salts, although more soluble than $\text{KCl} + \text{IrCl}_2$, do not dissolve easily in the crystallized state in water; notwithstanding they crystallize with difficulty from their solutions, and only when these are highly concentrated.

III. *Sesquichloride of Ruthenium and Sodium?*—This compound could not be obtained crystallized and in a state fit for analysis. It formed a semi-crystalline deliquescent mass, readily soluble in spirit, which dried when strongly heated, but then became partly green and blue, and behaved therefore like a mixture of chloride of sodium and sesquichloride of ruthenium. A solution of chloride of barium and Ru^2Cl^3 dried to a deliquescent mass, which resembled the preceding salt, but from which spirit extracted the sesquichloride of ruthenium, leaving behind chloride of barium.

IV. *Perchloride of Ruthenium and Potassium*, $\text{KCl} + \text{RuCl}_2$.—The conversion of Ru^2Cl^3 into RuCl_2 is very difficult. When treated for a long time with nitromuriatic acid, only a very small portion passes over into perchloride, and it is impossible to effect its complete conversion. When heated with muriatic acid and chlorate of potash, some of the salt is formed; but the greater portion of the ruthenium is lost, it being converted into a higher chloride (probably RuCl^3), which is volatile and escapes with the aqueous vapours. I unfortunately did not make this observation before I had already consumed most of the ruthenium, and did not possess sufficient to examine more closely this interesting compound.

I once obtained the perchloride accidentally, having added by mistake too much nitric acid in precipitating the oxide from the ruthenate of potash. The solution of the oxide in nitric acid filtered from the precipitated oxide was brown, and yielded, on evaporation with some muriatic acid, at first a considerable quantity of crystallized saltpetre; and on further concentration of the rose-coloured mother-ley a red salt crystallized, which, washed first with chloride of ammonium, then with spirit, was the compound in its pure state. The crystals of this salt are so minute that their form cannot be recognised with the naked eye; with a magnifying power of 300 times diameter they appear as perfectly transparent red prisms with pointed terminal surfaces, probably belonging to the rhombohedral system. The salt is readily soluble in water, insoluble in spirit of 0.889, and scarcely soluble in a concentrated solution of chloride of ammonium; its solution is of a rose colour playing into violet, and cannot be distinguished from that of the chloride of rhodium and sodium; it is scarcely affected by sulphuretted hydrogen, and only deposits after some time a little yellowish-brown sulphuret, without the liquid losing its red colour. If to the solution of this salt an alkali is added, no precipitate results, but on evaporation a yellowish-brown gelatinous hydrated oxide separates, which contains a con-

siderable quantity of alkali, and when heated on platinum explodes slightly with a sudden glowing. A concentrated solution of this salt in water is only partially precipitated by alcohol; the greater portion remains in solution with a red colour, and is not reduced to a lower chloride on evaporation. The blue reaction of the sesquichloride of ruthenium cannot be produced in the solution of this salt even when sulphuretted hydrogen is passed through it for six hours. The metal reduced from this salt is ruthenium, for it yielded on ignition with nitre ruthenate of potash, and this with muriatic acid sesquichloride of ruthenium, in which the blue reaction could be produced by sulphuretted hydrogen.

Sulphurets.

It is highly probable that as many combinations of ruthenium with sulphur exist as this metal forms oxides, but their preparation is accompanied with numerous difficulties. When, for instance, powdered ruthenium is mixed with sulphur and heated in an atmosphere of carbonic acid, there is no appearance of any chemical reaction, the sulphur distils off, and the ruthenium increases but little in weight. The precipitates obtained from the chlorides by sulphuretted hydrogen by no means correspond to those compounds; they always contain too much sulphur, and are very probably mixtures of sulphurets with sulphur; their analysis is very difficult, as they easily become oxidized in drying, and are partially converted into sulphate. When heated, in order to remove the water, they explode faintly with incandescence; and when treated with fuming nitric acid, they are likewise oxidized with a faint explosion and a shower of sparks. They dissolve, it is true, in ordinary nitric acid very easily, but the sulphuric acid formed cannot be precipitated pure from this solution by a salt of baryta; it is coloured yellowish, and always contains some sulphate of ruthenium, which cannot be removed by any solvent. When the sulphuret precipitated from the sesquichloride is heated in a reduction-tube through which carbonic acid is passed, water and sulphur are removed, accompanied by a glowing and explosion, and the blackish-gray metallic powder left yields results which correspond to the formula Ru^2S^3 . The sulphuret which is precipitated when sulphuretted hydrogen is passed for a short time through the solution of Ru^2Cl^3 , frequently contains 3 atoms of sulphur to 1 of ruthenium; but if the gas has been passed through for several hours, a sulphuret, RuS^2 , of yellowish-brown colour, is obtained. Sulphuret of ammonium throws down a blackish-brown sulphuret, Ru^2S^3 , from the blue protochloride; however, I place little value on these analyses, as the difficulties render the results very uncertain.

Oxysalts.

I have little experience on this series of compounds, as their preparation is very difficult, and my material was consumed; I only obtained the sulphate of ruthenium, $\text{RuO}^3 + 2\text{SO}^3$, from the sulphuret, which is formed on treating Ru^2Cl^3 with sulphuretted hydrogen by oxidizing it with ordinary nitric acid. An orange-coloured

solution is obtained, yielding on evaporation to dryness a yellowish brown amorphous mass, which attracts moisture, deliquesces, and has an acid astringent taste. The dry compound reduced to powder resembles mosaic gold, dissolves readily in water, and is not precipitated at first by alkalies; but on evaporation the yellowish-brown gelatinous hydrated oxide separates, which has the greatest resemblance to the impure oxide of rhodium, and explodes with incandescence when heated. Sulphuretted hydrogen does not produce the blue reaction in the solution of this salt.—Liebig's *Annalen* for August 1846.

Some Experiments on Assafœtida. By H. REINSCH.

An ounce of finely pulverized assafœtida was mixed with an equal weight of hydrate of lime, and then stirred into a thin paste with a sufficient quantity of water. On submitting this to distillation, a colourless oil passed over with the water, and at the same time some ammonia was disengaged. The oil possessed a burning taste, and an odour differing from that of assafœtida. The residue in the retort was collected on a filter, and washed with hot water until this passed through colourless. A portion of the filtered solution was supersaturated with dilute sulphuric acid, when some brown flakes separated, which united on warming to brown drops, while upon the surface of the liquid some oil collected. On distilling this mixture, some traces of sulphuretted hydrogen, a slightly acid water and some drops of oil passed over. Neither valerianic nor angelic acid could be detected in it. The residue left in the retort was brittle, dissolved readily in ammonia, æther and alcohol, from which it separated as a grayish powder. The alcoholic solution of the resin has a faintly acid reaction. When heated on platinum it melts, and then burns with a bright flame; heated in a glass tube, it disengages white vapours, and subsequently drops of a green oil; at the same time the odour of horse-radish is perceptible. Concentrated sulphuric acid dissolves it with a brown colour, from which it is precipitated by water. Precipitated from the lime solution by muriatic acid, the resin forms a greenish powder, which does not cohere, but in its other properties it agrees with that precipitated with sulphuric acid. When the lime residue with which the assafœtida has been treated is exhausted with spirit, a yellow tincture is obtained, which has the taste of assafœtida, but is not bitter like the above resin. If the tincture be mixed with an acid, a resin separates, which possesses the peculiar odour of assafœtida.—*Jahrb. für Prakt. Pharm.*, xii. p. 362.

On the Composition of the Salts of Antimony. By M. PELIGOT.

Among the consequences deduced from the theory of chemical proportions, as established by the fertile discoveries of Wenzel and Richter, one of the most important and most useful has undoubtedly

been the law advanced by Berzelius, in reference to the simple relations which exist between the oxygen of the acid and the oxygen of the base of any salt. It is known that, taking this law for basis, and determining the quantity of base and acid requisite to form a truly neutral salt, as the sulphate of potash, we have been led to admit that the quantities of the different bases saturating a given weight of the same acid, must contain the same quantity of oxygen. This law however has not been found to hold good in some cases. In my memoirs on uranium and the compounds of this metal, I have shown that the sesquioxide of uranium, $U^2 O^3$, forms salts which possess all the characters which are generally attributed to neutral salts, notwithstanding that it combines with a single equivalent of acid; these salts would be, according to the law of Berzelius, tribasic; but there does not exist a salt of uranium containing 3 equivs. of acid, conforming therefore in its composition to the conditions of the law of composition of neutral salts.

The present investigation shows that the salts of the sesquioxide of antimony, $Sb^2 O^3$, present the same peculiarity as the salts of uranium. Hitherto the salts of antimony have been but little studied; they are, it is true, difficult to prepare, owing to the decomposing action which water exerts on the majority of them; nevertheless by employing certain precautions I have succeeded in obtaining in a pure state the following:—

Sulphates of antimony	$\left\{ \begin{array}{l} 4SO^3, Sb^2 O^3, HO. \\ 2SO^3, Sb^2 O^3. \\ SO^3, Sb^2 O^3. \\ SO^3, 2Sb^2 O^3. \end{array} \right.$
Subnitrate	$NO^3, 2Sb^2 O^3.$
Oxalate	$2C^2 O^3, Sb^2 O^3, HO.$
Oxalate of potash and antimony....	$7C^2 O^3, Sb^2 O^3, 3KO, 8HO.$
Crystallized tartrate	$2C^8 H^2 O^8, Sb^2 O^3, 13HO.$
Tartrate precipitated by alcohol ..	$C^8 H^2 O^8, Sb^2 O^3, 2HO.$
Bitartrate of potash and antimony..	$2C^8 H^2 O^8, Sb^2 O^3, KO, 8HO.$

From these formulæ it results that the sesquioxide of antimony, like the oxide of uranium, forms salts, the true composition of which is by no means conformable to that which theory had *à priori* assigned to them; so that for these two classes of salts all the formulæ which are met with in the tables of equivalents are inaccurate. In fact I have found it impossible to prepare a single salt of antimony containing 3 equivs. of acid to 1 of base, that is to say, a neutral salt of antimony, according to the law of M. Berzelius.

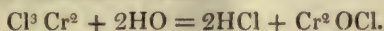
The sesquioxides of antimony and uranium have consequently a capacity of saturation peculiar to them, which differs from that of the other sesquioxides as those of aluminium, chromium, and even of bismuth; for I have convinced myself that the analogy existing between this last metal and antimony is not continued in the saline compounds formed by their oxides; for the sulphate of bismuth is $3SO^3 Bi^2 O^3, 3HO$; the nitrate, $3NO^3, Bi^2 O^3, 10HO$; the oxalate, $3C^2 O^3, Bi^2 O^3, 6HO$, &c. These results may be interpreted in different ways; it may simply be admitted that the salts of antimony

and uranium are proportional to the ordinary salts formed by the monoxides, U^2O^3 and Sb^2O^3 being equivalent to the oxides of the form RO . But this hypothesis is opposed to the law of the constitution of salts; and I prefer admitting for the oxide of antimony, as well as for the oxide of uranium, the existence of an oxidized radical U^2O^2 , Sb^2O^2 , which combines with 1 equiv. of oxygen, yielding an oxide of the nature of the ordinary protoxides; this oxide consequently unites with 1 equiv. of acid to produce a neutral salt, and we have—

Oxide of antimonyle	$(Sb^2O^2)O$.
Chloride of antimonyle (powder of algaroth)	$(Sb^2O^2)Cl$.
Sulphate	$SO^3(Sb^2O^2)O$.
Oxalate, &c.	$C^2O^3(Sb^2O^2)O + C^2O^3 + HO$.

This hypothesis of an oxidized radical has not, it is true, met with the sanction of M. Berzelius; after having strongly opposed it, in reviewing my first researches on uranium, the illustrious Swedish chemist returns to this discussion in his last annual report, in noticing my second memoir on this subject. He states that my observations on the combinations of the oxide of uranium agree perfectly with the reactions of this oxide with the bases of the form R^2O^3 , and that they would lead to the conclusion that all the oxides of this form are composed of 1 atom of oxygen and of a compound radical, which is itself formed of 2 atoms of the inferior oxide; he then passes a severe judgement on this theory, which however I trust is not beyond appeal, and in the mean time I may take the liberty of making a few observations on this subject. In the first place, M. Berzelius goes against evidence in seeking to prove, as he has done for several years, that *all* the oxides of the form R^2O^3 form salts which are at the same degree of saturation. Among these oxides there are *at least* two, the oxides of uranium and antimony, which combine in preference with 1 equiv. acid, and which *never* combine with 3 equivs., at least according to the analyses which have hitherto been made. The salts formed by these oxides consequently render the law of M. Berzelius on the constitution of salts defective. It is in order to preserve this law in all its force, that I have proposed to admit that in these oxides the third of the oxygen alone determines their capacity of saturation, the other two-thirds being masked as it were in a hypothetical radical. I can perfectly understand why this interpretation is not admitted; but in what is it so absurd, as M. Berzelius states? Certainly not because it compels us to admit that an oxide may contain oxygen in two different states; sufficient examples exist to prove by analogy that such may be the case. The researches of M. Regnault on the action of chlorine upon the Dutch liquid, met with the universal approbation of chemists; and they clearly prove that, in the various compounds which he studied, a portion of the chlorine must be considered as existing in the form of hydrochloric acid, whilst another portion constitutes with the carbon the organic radical. Has not M. Cahours shown,

in a recent investigation, that the properties of perchloride of phosphorus lead to this body being considered as a compound of protochloride of phosphorus and chlorine? Have I not proved by experiments, the results of which have not been called in question, that the sesquichloride of chromium, once dissolved in water, does not yield more than two-thirds of the chlorine it contains to nitrate of silver? and does not this fact show most distinctly that in this binary compound the 3 equivs. of chlorine are not combined with an equal affinity? Can it be otherwise when the following reaction is obtained under the influence of water?—



What is true for a chloride may also be admitted for an oxide, without incurring the whole of M. Berzelius's disapprobation.

It must moreover be observed, that this hypothesis relative to the existence of these oxidized radicals is only useful as far as the law of M. Berzelius on the constitution of salts really exists. But if it be admitted that this law does not rest on any solid foundation, that it is only the expression of numerous facts, the greater number of oxides containing a single equivalent of oxygen; that it proves deficient when applied to a class of oxides, which I have no doubt will be rendered more numerous by subsequent researches; if it be admitted that these oxides combine with proportions of acids, which are determined by a property peculiar to them, in the same way as we admit at present monobasic, bibasic acids, &c., the hypothesis of these radicals becomes useless. Until this opinion be adopted, I persist in believing that the supposition of these oxidized radicals furnishes the best means of making M. Berzelius's law agree with the composition of the yellow salts of uranium and the salts of antimony.—*Comptes Rendus*, Oct. 12, 1846.

Platinum in the Oxidized State. By G. OSANN.

Water, which was perfectly free from salts of sulphuric and muriatic acids, was decomposed by a battery; after this had been carried on for some time, the platinum wire which had formed the positive electrode was removed, and placed in contact with paste containing iodide of potassium. A faint, but distinctly visible reaction of iodide of starch resulted. In another experiment some platinum sponge was boiled with caustic potash, then washed with hot water and dried. Pure oxygen, obtained from chlorate of potash, was passed over it in a glass tube, and the spongy platinum heated by a lamp placed under the glass tube. The tube was then allowed to cool, and the spongy platinum left for 24 hours in contact with the oxygen. On triturating the spongy platinum with iodide of potassium and starch, it became black after a time from the formation of iodide of starch. An analogous experiment with ordinary sponge of platinum did not yield the same result. This agrees with what De la Rive found, viz. that a piece of platinum foil, which had served for some time as a positive electrode in water, disengaged

less hydrogen when it was subsequently used as a negative electrode, from a portion of the hydrogen being consumed in the deoxidation of the platinum foil. As in the above action of the platinum upon the iodide of potassium paste, the oxygen at the surface of the platinum cannot be the active agent, it is most probable that some acid is formed, which produces the decomposition of the iodide of potassium.—Poggendorff's *Annalen*, lxvii. p. 374.

On the Reciprocal Action of Metals and Concentrated Sulphuric Acid. By E. MAUMENÉ.

The action of concentrated sulphuric acid on the metals at a gentle heat is in general very simple, and is represented by the equation $M + 2SO^3 = MOSO^3 + SO^2$; however, the facts are not always as simple as the theory, and in some cases their complication is truly surprising.

When copper and sulphuric acid are heated, there is formed sulphurous acid and sulphate; but at the same time a black powder, perfectly similar in appearance to the binocide of copper. This fact is well known; and M. Barruel, who examined this powder, considered it to be sulphuret of copper. Two years ago I had occasion to prepare large quantities of sulphurous acid by means of copper, and my attention was naturally directed to this accidental sulphuret, and I ascertained that its formation is not the result of a simple action. The moment the decomposition of the sulphuric acid is intimated by the disengagement of the sulphurous gas, a brown powder is deposited, which is the protosulphuret of copper. This protosulphuret once formed does not remain long unchanged, it becomes black; and if the operation be discontinued after the disengagement of a certain quantity of sulphurous acid, in order to collect the insoluble product, and submit it to analysis, very different but readily explicable results are obtained. The protosulphuret, after its formation, soon combines with some oxide of copper to form a compound $Cu^3 S^2 O = 2Cu^2 S CuO$; this subsequently loses 2 equivs. copper, and becomes $Cu^3 S^2 O = 2CuSCuO$; and the latter lastly combines with some oxide of copper, so that the final product is generally composed of sulphuret and oxide of copper in equal equivalents, viz. $2CuSCuO + CuO = 2(CuSCuO)$. It is easily conceived that it is not possible to isolate at will any one of these bodies in a state of perfect purity. It is in preparing numerous products, in operations which I discontinued after the disengagement of the fourth and fifth part of the sulphurous acid, and submitting all these products to analysis, that I have been able to discover, and in some measure follow step by step, these unforeseen modifications. The formation of the protosulphuret, and consequently of the oxysulphurets above-mentioned, never occurs to a great extent. The quantity of copper which passes into the state of sulphate is about 50 times that of the copper contained in the oxysulphuret.

Lead is acted upon in the same manner; the sulphate which is

deposited is always strongly coloured gray by the sulphuret. Bismuth, tin, antimony and arsenic do not exhibit a trace of sulphuret, but towards the end of the operation a small quantity of sulphur is always observed to condense on the cold parts of the vessel; nor could I detect the presence of sulphuret on operating on a small quantity of silver. I believe that the formation of sulphuret and oxysulphuret are sufficiently explained by the great affinity of the sulphur for the metals. At the commencement of the operation a small quantity of the sulphuric acid is decomposed by the metal, which deprives it of its oxygen and its sulphur at the same time.—*Comptes Rendus*, Sept. 7, 1846.

On the new Metal Ilmenium. By M. HERMANN.

This new metal was discovered by M. Hermann in a mineral which he supposed at first to be ytthro-columbite, but which he now proposes to call ytthro-ilmenite, since it contains no columbic acid. The ilmenium which occurs in this mineral is in a form that has many characters in common with columbic acid, but is distinguished from it by several others; for example, the density of ilmenic acid is much less than that of columbic acid; it becomes very yellow by calcination; its hydrate, moistened with hydrochloric acid, assumes a blue colour when in contact with zinc; and it expels when fused with carbonate of soda a much larger proportion of carbonic acid. In the same way, ilmenic acid is distinguished from niobic acid, by the perfect insolubility of its hydrate in concentrated hydrochloric acid, and by its giving no colour to glass by the blowpipe.

A characteristic property of ilmenic acid is, that a solution of ilmenate of soda gives with a mixture of hydrochloric acid and tincture of galls, or ferrocyanide of potassium, precipitates which are of a much deeper brown colour than hydrate of iron; neither columbic nor niobic acid gives a precipitate of so deep brown a colour. The atomic weight of ilmenium is not so great as that of columbium and niobium. If it be admitted that ilmenic acid contains two atoms of oxygen, the atomic weight of ilmenium will be $753 \cdot 0 = 11^2$.

The preparation of ilmenic acid from ytthro-ilmenite is effected by reducing the mineral to fine powder and fusing it with six times its weight of bisulphate of potash, till a limpid solution is obtained; this is to be treated with boiling water, so as to leave an insoluble subsulphate of ilmenium.

To be sure that none of the mineral remains undecomposed, the subsulphate of ilmenium is to be again fused with bisulphate of potash and treated as before. After having well-washed the subsulphate, it is to be moistened, without drying, with hydrosulphate of ammonia, and digested with it; it is then to be washed, boiled with concentrated hydrochloric acid, again washed and dried. These operations yield subsulphate of ilmenium, which when heated in a forge, gives pure ilmenic acid.

Metallic ilmenium is obtained by calcining in an atmosphere of

ammonia, the ammonio-chloride of ilmenium, in the same manner as employed in reducing niobium. It forms porous particles or cohering laminæ having the black appearance of soot, or of the charcoal produced by the burning of sugar. Ilmenium does not decompose water; neither nitric nor hydrochloric acid nor aqua regia, even when boiling, acts upon ilmenium; when heated in the air it takes fire, burns and yields white ilmenic acid.

Ilmenic acid is therefore obtainable by three processes,—by the combustion of ilmenium, the calcination of hydrate of ilmenium, and the calcination of subsulphate of ilmenium in a forge. When obtained by the first or third method, it has the form of perfectly white fragments, with an earthy fracture; these fragments possess but slight cohesion, for by the slightest pressure, or by moistening with water, they are reduced to a soft powder. The acid prepared by the second process forms white firm masses which have a conchoidal fracture and no lustre.

During calcination, ilmenic acid assumes a fine golden tint; and the acid obtained from the hydrate becomes, under these circumstances, of a deeper colour than the acid prepared by calcining the subsulphate. On cooling, the ilmenic acid resumes its white colour perfectly. Its specific gravity is from 4.10 to 4.20.

Hydrated ilmenic acid is precipitated when excess of hydrochloric acid is added to a solution of ilmenate of soda; it is a white, diaphanous and gelatinous precipitate, which dries in opaque compact pieces.

Ilmenic acid does not dissolve in concentrated sulphuric acid, but at a red heat it fuses readily with bisulphate of potash or soda, yielding a limpid product which is yellow while hot and becomes colourless on cooling. After washing this product, the ilmenic acid remains perfectly insoluble, in combination with sulphuric acid, forming a thick white precipitate, which leaves on drying white pieces of an earthy fracture.

Ilmenic acid has but slight affinity for sulphuric acid; by long-continued washing it separates from it perfectly, and is converted into hydrate.

A portion of sulphate of ilmenium, the last washings of which still retained traces of sulphuric acid, was dried at 122° F.; and was then found to consist of ilmenic acid 77.63, sulphuric acid 7.69, water 14.68.

Subsulphate of ilmenium even while moist is totally insoluble in hot concentrated hydrochloric acid; this property distinctly marks the difference between ilmenic and niobic acid. Subsulphate of ilmenium readily loses the whole of its sulphuric acid at a red heat.

Chloride of ilmenium is prepared like the chloride of columbium; it is deposited in the cold part of the porcelain tube like hoar-frost, composed of yellowish translucent prisms; in a moist atmosphere this salt exhales hydrochloric acid vapours; it then becomes white and opaque; when thrown into water it is decomposed, with the evolution of much heat, and with the production of hydrochloric acid

and diaphanous colourless flocks of hydrated acid. It absorbs ammonia with great avidity and the disengagement of considerable heat; a yellow mass is also produced, which by calcination *in vacuo* is converted into hydrochlorate of ammonia and ilmenium.

Equal parts of ilmenic acid and dry carbonate of soda, heated strongly to redness, lost carbonic acid equal to 29.1 per cent. of the weight of the ilmenic acid.

Ilmenate of soda is a gray mass with an earthy fracture; when boiled in water it is decomposed into soluble subilmenate of soda and a superilmenate which is deposited in the state of a white powder.

Excess of either nitric or hydrochloric acid completely precipitates the ilmenic acid from ilmenate of soda; this circumstance distinguishes it essentially from columbic and niobic acids, which remain partly in solution.

A concentrated solution of ilmenate of soda does not yield crystals by spontaneous evaporation; the solution becomes gradually turbid by the action of the carbonic acid of the air, and deposits a white powder of acidulous ilmenate of soda.

When ferrocyanide of potassium, and afterwards hydrochloric acid, are added to a solution of ilmenate of soda, a precipitate of a deeper brown colour than hydrate is produced; tincture of galls acts similarly.

Hydrate and subsulphate of ilmenium do not dissolve in acids; acid solutions of ilmenic acid cannot therefore be prepared for the purpose of acting upon zinc; but if the hydrate or subsulphate recently precipitated be moistened with hydrochloric acid, and then exposed to the action of zinc, a grayish-blue colour is produced.

With borax and with a phosphate, ilmenic acid produces glass both in the interior and exterior flame of the blowpipe, which appears to be yellow, but which becomes colourless on cooling. This metal is so named from the Ilmen mountains near Miask, in which the mineral containing it is found.—*Journ. de Pharm. et de Ch.*, Octobre 1846.

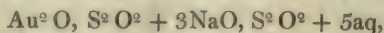
[It is very probable that this new metal may prove to be nothing more than pelopium described at page 349. In a communication with which we have been favoured, Prof. Rose states "that he cannot venture to decide in what relation the ilmenic acid stands to pelopic acid, from the few properties which M. Hermann has described. According to him, ilmenic acid acquires a golden-yellow colour on ignition, while pelopic acid, according to my experiments, only becomes yellowish. The most important character of ilmenic acid, by which it differs essentially from columbic and niobic acids, is said to be that it is precipitated entirely by hydrochloric acid from the solution of its soda salt; while pelopic acid, according to my experiments, when precipitated by hydrochloric acid from a solution of the pelopate of soda, is dissolved in an excess of the acid to an opalescent liquid, in which no precipitate is formed by boiling. According to Hermann, the solution of the ilmenate of soda is rendered turbid by the influence of the carbonic acid of the atmosphere, which I have not observed to be the case with the pelopate of soda. The quantity of carbonic acid which, according to Hermann, is expelled from the

carbonate of soda by fusion with ilmenic acid, is entirely different from that which is expelled under similar circumstances by pelopie acid. Tincture of galls produces, according to Hermann, in a solution of the ilmenate of soda to which some hydrochloric acid has been added, a brown precipitate; that formed under similar circumstances in pelopate of soda, according to my observations, is orange-yellow. The beads produced in the inner and outer flame before the blow-pipe, by ilmenic acid with borax and microcosmic salt, are yellow while hot and become white on cooling, which does not agree with the behaviour of pelopie acid towards the same reagents. Lastly, the specific gravity of ilmenic acid, as stated by M. Hermann, does not agree with that which I have found for pelopie acid."—W. F.]

On two new Series of Double Salts containing Protoxide of Gold.
By C. HIMLY.

Although, according to Mitscherlich, metallic gold dissolves in selenic acid, the existence of a salt of selenious acid, supposed to be formed, is still very problematical, and certainly not at all proved. The existence of a fulminate of gold is likewise doubtful, and that explosive compound would probably allow of being considered under a different point of view. We are consequently unacquainted with any true oxysalt of gold; it will therefore not be uninteresting to become acquainted with two new series of gold salts, and indeed protosalts, which hitherto have, it is true, not been isolated, but occur in well-characterized double salts. The two acids forming these double salts are precisely such as we should least expect it from, judging from their other chemical properties; they are the monothionous and dithionous acids. The behaviour of dithionous acid towards metallic oxides, in those proportions in which double salts are formed, is altogether very peculiar, and may probably serve to throw considerable light on the constitution of salts.

The formula of the double dithionite is



and the oxygen of the water + that of the soda is equal to that of the acid; the oxygen of the protoxide of gold and soda is half that of the acid.

The soda salt of the double monothionite has a similar composition, and is perfectly colourless in solution; it is precipitated by alcohol, appears yellow like fulminating gold by reflected light, and red like gold-purple by transmitted light. It yields a precipitate with nitrate of silver of the colour of chromate of lead, and with salts of lead a red perfectly-insoluble compound.

I have already prepared and examined a large number of compounds of this kind, but am prevented at present from completing the investigation, which I hope however soon to publish.—*Liebig's Annalen*, July 1846.

ANALYTICAL CHEMISTRY.

On the Determination of the Amount of Starch in the various kinds of Vegetable Food. By Dr. KROCKER.

It is scarcely possible to determine accurately the amount of starch in any vegetable by mechanical means. The author has therefore proposed a method which consists in first converting the starch into sugar, and determining from the loss, the carbonic acid which escapes in the fermentation of the latter. He first convinced himself that in the different kinds of grain examined by him no sugar or dextrine pre-existed. When wheat, rye, &c. were extracted with water and edulcorated for a length of time, the residue on evaporation exhibited not a trace of dextrine and only a small quantity of sugar. When, on the contrary, the same kinds of meal were exhausted with lime-water, the lime removed by a current of carbonic acid, and the filtered solution evaporated in the water-bath, not a trace of sugar or dextrine could be detected in the residue; so that undoubtedly the former must have been produced in the preceding experiments by the action of the free acid; consequently the whole of the carbonic acid liberated in the fermentation could be referred to the starch.

In these experiments a certain quantity must be employed according to circumstances, as, on the one hand, with too much substance the fermentation lasts too long; while, on the other hand, when the quantities are too small, the errors of observation increase very considerably. It is most advantageous to mix a comparatively large quantity of yeast with little substance, always according to the probable amount of starch; for instance, with different kinds of meal, 3 grms.; with potatoes, 6 to 8 grms. The weighed quantity is heated with water in a porcelain dish until it has become softened; then about 15 drops of sulphuric acid, diluted with 5 parts of water, added to it, in order to convert the starch into sugar. It is ascertained from time to time whether the conversion is complete, by treating a drop of the mixture upon a watch-glass with some solution of iodine, but then carefully washing it again into the original mixture. As soon as the colour of the mixture is no longer turned blue or vinous red by solution of iodine, the entire mass is evaporated to the consistence of a syrup, and conveyed into one of the small flasks of Will and Fresenius's alkalimetric apparatus*. In this apparatus the liberated carbonic acid passes, as in the examination of pearlsh, into a second flask, where it is freed by concentrated sulphuric acid from aqueous and alcoholic vapour; but the tube which dips into the mixture itself must not be closed, as otherwise it readily happens that the acid ascends. It is also well to have the flask which is to contain the fermenting mixture of a larger size, and that for the sulphuric acid as small as possible. Now after the mass has been conveyed into the larger flask, the free acid must

* A description of the process, with an engraving of the apparatus, will be found at page 637 of the first volume of this Journal.

be neutralized; for which purpose the author uses a very concentrated solution of tartrate of potash, which he adds in quantity corresponding to that of the acid; the bitartrate of potash which is thus formed moreover favours the fermentation. To set this in action, about 20 grms. of fresh yeast are added to the mass thus prepared, the carbonic acid existing in which is determined by a separate experiment. The apparatus is then exposed to a constant temperature of 77° F. After 4 or 5 days the decrease in weight of the apparatus scarcely amounts to 0.001 gm., and the experiment is finished. To be certain, however, a fresh weighed quantity of yeast is added, in order to see whether any further decrease in weight results within 24 hours. It is even advantageous to add some weighed yeast after the first 48 hours. The carbonic acid, found by the loss in weight after deducting that contained in the yeast, represents the starch $C^{12}H^{10}O^{10}$, which is converted by taking up 2 equivs. HO into $C^{12}H^{12}O^{12}$, and then into $4CO^2$ and $2C^4H^6O^2$. An experiment was made with perfectly pure starch prepared from beans; 2.544 grms. yielded 1.31 carbonic acid. The 20 grms. yeast added to it contained 0.16 gm. carbonic acid, which left therefore for the starch 1.16, corresponding to 83.52 per cent.; or, after deducting 16.26 per cent. water, gives 99.69 per cent. starch.—Liebig's *Annalen*, lvii. p. 212.

Observations on the Determination of Nitrogen in Organic Bodies.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,—The following communication is of no further importance than as containing the results of considerable experience in the admirable mode proposed by MM. Varrentrap and Will for determining the amount of nitrogen in organic bodies. By drawing attention to a few sources of error in manipulation, particularly in a certain class of bodies, I hope to lessen the chance of failure and prevent the annoyances which result from the loss of an analysis. The mode alluded to, as is well known, may be said to consist of four stages:—1st, the combustion; 2nd, the collecting the ammonia formed in a bulb-receiver; 3rd, the careful removal of the muriate of ammonia, precipitation with chloride of platinum, and evaporation; 4th, the transference of the platino-chloride into a filter, and subsequent operations necessary for determining the amount by weighing. With reference to the first stage, it is of importance to pay much attention to the proportion of the hydrate of soda and lime. The original proportions, of 1 part of hydrate of soda to 2 parts of lime, answer well enough for ordinary cases; it however occasionally happens that the body to be analysed contains a small quantity of nitrogen to a large quantity of hydrogen. Two incidents result from this constitution; in the first place, we use a large quantity of substance, to reduce the chances of manipulatory error to the lowest limit; and, as a necessary consequence, the amount of hydrogen being proportionally increased, a large quantity of water is formed during the combustion. The result is, that the moisture being driven to the

cooler portion of the tube, converts the soda-lime into a soft pul-taceous mass, which in time plugs up the tube to the inevitable loss of the analysis. Sometimes, and most generally, this happens towards the open end of the tube, but if we escape this accident another awaits us. A barrier of the semi-fluid mixture is formed at the portion of the tube which is drawn out, and we are not able to remove the whole of the ammoniacal gas at the end of the operation; and, in the case we are supposing, as much as one-third of the ammonia may be lost. I have found the following precautions sufficient to remove all risk, and can safely affirm that, by adopting them, I have not lost a nitrogen analysis for the last two years. The proportions of the mixture I use are 1 part of the hydrate of soda to 4 parts of lime; in forming the combustion-tube, instead of abruptly drawing up the angular portion, it is first drawn out for about a quarter of an inch, and then upwards, forming in fact a segment of a circle instead of an abrupt angle. In loading the tube, I first introduce coarsely-powdered lime for the space of an inch.

I beg now to direct attention to another source of error, which I believe to have in some cases occasioned the discovering nitrogen in bodies perfectly free from that element. We have seen 2 per cent. found in crystallized cane-sugar. It is well known that if two vessels, the one containing solution of ammonia, the other hydrochloric acid, be placed near each other, chloride of ammonium is rapidly formed in the vessel containing the acid. Now, in a large laboratory, however careful an operator may be, his results are in no small degree under the control of his neighbour; and the accident to which I have alluded may occur during the lengthy process of evaporation; in a private studio such an event can scarcely happen.

I remain, Sir,

St. John's, Isle of Man,
Nov. 4th, 1846.

Your very obedient Servant,
GEO. KEMP, M.D. Cantab.

On the Estimation of Tin by Volume.

By M. GAULTIER DE CLAUVERY.

The normal solution which I employ is formed of 1 grm. of iodine to the decilitre of alcohol of 0.932; and the solution of tin is prepared with 1 grm. of this metal, dissolved in hydrochloric acid, diluted with water freed from air, so as to form 1 litre. By means of M. Gay-Lussac's pipette, a demidecilire of the tin solution is measured off, and the burette, divided into tenths of a cubic centimetre, is filled with the normal solution; the latter is poured into the first until it is no longer decolorized; half a decilitre of the tin solution, containing 5 decigrms. of tin, decolorizes 100° or 10 cubic centimetres of the normal solution. If the tin ore under examination is soluble in hydrochloric acid, the operation is perfectly simple; if it does not dissolve in it, it is acted upon with *aqua-regia* containing much hydrochloric acid; and when the tin is become converted into perchloride, an excess of hydrochloric acid is added, and it is then

boiled with some iron, which reduces it to protochloride; the process is now the same as in the preceding case. If it happens to be an alloy containing only 20 per cent. lead, hydrochloric acid will dissolve it; beyond that, however, only imperfectly; but as *aqua regia* scarcely acts on the compounds of lead, the alloy must be dissolved in nitric acid, evaporated to expel the excess of acid, and then treated with hydrochloric acid and iron. Stannic acid, especially when it has not been dissolved, is readily converted into protochloride in the presence of an excess of hydrochloric acid and protochloride of iron, so that the assay is brought to the same state as when the product could be acted upon immediately with hydrochloric acid. When the compound to be analysed contains one of the following metals, arsenic, antimony, bismuth, copper, lead or mercury, the iron precipitates it, and again reduces the assay to the state of a tin solution.

To precipitate the whole of the copper, and not to leave any of the protochloride of that metal in the solution, a considerable excess of hydrochloric acid must be employed, and the boiling with iron continued for some length of time. The analysis of a salt of tin can be made with the same ease; and if a mixture of a per- and protosalt is examined, or any of the corresponding haloid compounds, the relative proportions can be determined by analysing the substance itself, and then making a second analysis of the product boiled with hydrochloric acid and iron.

Greater accuracy may be obtained by employing a decime solution of iodine; or rather, instead of using a pipette representing 5 hundredths of tin, only four are employed, equal to 2 decigrammes, or rather 10, equal to 5 decigrammes of metal; it is then possible to make two comparative assays with the litre of solution.

Zinc and iron do not interfere in the analysis by iodine, while the protosalts of iron, or the corresponding haloid compounds, decolorize the sulphate of indigo, which M. Pelouze had attempted to employ for the estimation of tin, and render this process impracticable.

I first used zinc to restore the tin to the state of protochloride; but iron is preferable, because it does not precipitate any tin, which, although very soluble in an excess of hydrochloric acid, requires for solution a somewhat long boiling with the acid. The alcoholic solution of iodine becomes altered in the course of time; so that before employing it, its strength should be determined by dissolving 1 gm. of tin diluted so as to form 1 litre.

The solutions of iodine employed in some chirurgical cases seem to have produced very different results, which can only be explained by the different state of their contents, some containing iodine, others more or less hydriodic acid. The method which I propose will allow of readily determining the proportion, and the state in which the iodine exists in a solution.

Iodine may be used to determine the quantity of tin in a solution containing various metals; but if there be present an arsenite, sulphite or hyposulphite, phosphite or hypophosphite, the normal solu-

tion will be decolorized, as with protochloride of tin. It will be requisite therefore to oxidize these salts by nitric acid or chlorine, and to reduce the tin to the state of protochloride by means of iron.—*Comptes Rendus*, July 13, 1846.

CHEMICAL PREPARATIONS.

Method of ascertaining the Purity of the Commercial Iodide of Potassium. By M. BERTHET.

THE extensive employment of the iodide of potassium in medicine and its very high price have gradually led to its being mixed with several other salts of less value, such as sulphates, chlorides and bromides. The quantity of time consumed in a chemical analysis requiring weighings in order to detect the fraud, leads to its very frequently being passed unnoticed. I have endeavoured to find out a method both quick and accurate for determining the amount of the iodide, and I have been induced to prefer the precise reaction of an alkaline iodate upon this iodide in the presence of an acid. It is known in fact that in this case the two salts are decomposed and the whole of the iodine precipitated.

I took as starting-point in my experiments the iodate of soda, it being the most soluble of all, and easily obtained of great purity. M. Millon, in his investigation of the iodates, has pointed out this character of great solubility, and has shown that when heated to 284° – 302° it lost all the water it contained, and that it was now represented by equal equivalents of acid and base.

The iodide of potassium was prepared by forming tri-iodate of potash, saturating it with pure carbonate of potash, leaving however a slight excess of acid, and then calcining.

Having obtained the salts, I wished to ascertain within what limits the action took place; for which purpose I weighed off accurately a certain quantity of each, and dissolved them in an undetermined quantity of water. I then took the weight of my bottles empty and full, and obtained thus the total weight of the liquids contained in them. For the experiment I employed any known weight of the solution of iodide, and added to it gradually the acid solution of iodate; I noted down the quantity used to complete the operation, and obtained by a simple proportion the real weight of each of the salts. This mode of operating necessarily led to great accuracy, because always working with different quantities of liquid, I could not be guided by the quantity of the solution of iodate of the preceding experiment, but solely by the identical characters of the reaction, and thus arrive at the true numerical relations.

When iodate of soda is dissolved in water slightly acidulated with sulphuric acid, and a few drops of the solution are poured into the

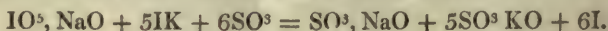
iodide of potassium, a precipitate is immediately produced, which redissolves on agitation, colouring the liquid; a further addition of iodate produces the same precipitate, which likewise redissolves; the liquid, which becomes more and more coloured by the ioduretted iodide formed, nevertheless remains of remarkable transparency; but a moment comes when a drop of iodate gives a slight turbidness, which no longer disappears on agitation, but gradually increases in proportion as solution of iodate is added; an abundant precipitation results, and the liquid becomes blackish to such a degree that it is difficult to perceive whether the iodate has produced any further reaction.

The iodine, from being in a state of great division, remains for a long time in suspension, which prevents it being seen whether the supernatant liquid still contains any undecomposed iodide. To obviate this I perform the precipitation in a flask, boil for a few minutes, when the whole of the deposited iodine is volatilized; the liquid becomes perfectly colourless, and by a measured addition of some drops of iodate we at last obtain a liquid which no longer becomes coloured; the whole of the iodide having become decomposed, nothing is left but the potash and the soda, combined with the sulphuric acid employed to acidify the iodate.

There are two periods to be observed in the precipitation,—the first is when the liquid, which though coloured is perfectly transparent, becomes suddenly turbid and of a brownish colour; the second when the liquid is no longer coloured by the addition of a drop of iodate.

Several experiments have shown under what circumstances decomposition ensues in these two periods. I will merely quote a few of the results. To obtain a complete decoloration of the solution of iodide of potassium, I employed 23·87 per cent. of the iodate; according to calculation it would be 23·875 per cent. To produce turbidness in the liquid I required on an average 11·55 per cent.

These results explain all the phases of the reaction. When iodate is poured into the iodide, iodine is liberated, which redissolves in the undecomposed iodide, and there is thus formed binioduretted iodide; a moment comes when the iodine can no longer be dissolved, and is precipitated, which renders the liquid turbid; it is found that, in order to attain this point, a little less than 1 equiv. iodate is required for 10 equivs. of iodide, and that decomposition is nearly half-effected. Subsequently, when the precipitation is complete, there is a very simple relation, that is to say 1 equiv. iodate is required for 5 equivs. iodide. Indeed, the equation is very readily established; the iodic acid parts with its oxygen to the potassium of the iodide, and the iodine of both salts is eliminated:—



None of the numerical results of the reaction experienced any perceptible variation from the presence of sulphates, chlorides or bromides, even in the proportions of 30 to 40 per cent. Bromide of potassium alone does not yield any precipitate with the solution of

iodate, but merely a very faint yellow colour, which is widely different from that of an ioduretted iodide.

It might happen that the iodide of potassium contained sulphurets and hyposulphites; but the least trace of these salts is immediately detected on the addition of the first drop of the solution of iodate of soda to the solution of such an iodide. In this case, instead of a precipitate of iodine, which redissolves immediately, and which is followed by the coloration produced by the ioduretted iodide, a turbid milky-white liquid is obtained, which is produced by an abundant deposit of sulphur.

In order to facilitate the use of this iodometric process, I have compounded my liquids so that instruments as precise as those described by M. Gay-Lussac for examining sodas and pearlashes, and which are found in every laboratory, may be employed; as, a graduated tube capable of holding 500 cubic centimetres, a pipette of 100 cubic centimetres capacity, an alkalimetric burette divided into cubic demicentimetres, and a small flask with a somewhat narrow neck capable of holding about 200 grms. The normal liquor of iodate of soda is made thus:—

Very pure iodate of soda	4·780 grms.
Pure sulphuric acid	15·000 ...
Distilled water sufficient to form 1000 grms. of liquid.	

50 cubic centimetres of this liquid, or 100 divisions of the alkalimetric burette, completely decompose 100 cubic centimetres of solution of iodide of potassium, made in the proportion of 5 grms. of iodide to 500 cubic centimetres of solution. The pipette therefore exactly holds 1 gm. of pure iodide, and requires for its decomposition 100 divisions of normal liquid. Each division less employed will denote 1 per cent. of foreign matter, and each drop approximatively two-thousandths, and a drop is readily appreciated.

Since each division of the burette decomposes a fixed quantity, that is to say 1 centigramme of iodide of potassium, it will always be easy, with a given solution of iodide, to ascertain the real quantity of iodide from the number of divisions employed to produce complete decomposition.

The experiment is made in the following manner:—After having weighed off 5 grms. of the iodide to be examined, it is dissolved with great care in the tube so as to have 500 cubic centimetres of liquid; a pipette-full is then taken and poured into a small flask holding about 200 grms. Holding the flask in one hand, the normal liquor with which the burette has been filled is gradually added with the other hand; on the addition of each drop it is requisite to agitate, in order to redissolve the precipitate; when evident turbidness results, the number of divisions employed is read off; and as experiment has shown that at this period the decomposition is about half-effected, an equal number of divisions to that employed to produce this turbidness is subsequently added at once; it is slightly agitated, to prevent the iodine, which is now precipitated in quantity, from caking together, and the flask is placed over a small fire or a spirit-

lamp. After 2 or 3 minutes' boiling the iodine is expelled, the liquid is colourless, and the reaction being nearly finished, only 1 drop of the normal solution is added, which no longer yields any precipitate, but merely a colouring, which very soon disappears on applying heat to the flask; each drop is now added with precaution until there is but a very faint yellow colouring, which proves that the decomposition is complete.

At this period 1 drop of the normal liquid leaves the solution perfectly colourless, the whole of the iodide is decomposed, the iodine volatilized, and the flask contains nothing but sulphate of soda and potash plus the drop of iodate last added, and which may be rendered evident by adding a little of the solution of the iodide.

Several commercial iodides have been analysed by this process, and I soon found a considerable difference in their purity. Some of them, notwithstanding their beautiful external appearance, and the efflorescent cubic form of their crystals, scarcely indicated 90 per cent. of pure iodide; that which appeared to me the purest of all was an iodide in small, transparent, very white laminae, for which I am indebted to the kindness of M. Quesneville. This iodide indicated 99 per cent., that is to say, it was nearly chemically pure.

In case merely approximative but quick results are desired, the first period of the reaction may suffice, and the turbidness resulting in the liquid taken as point of comparison. The experiment may be made in an ordinary glass cylinder, when the tint will be better distinguished than in a flask. A pipette of the solution of the iodide above-mentioned, representing 1 grm. of iodide, requires, in order to be rendered turbid, 48 divisions of the burette; each division that it requires less will indicate nearly 2 per cent. of foreign matter, and each drop nearly $\frac{1}{2}$ per cent.

Where the shade of colour alone is depended on, it is impossible to avoid errors of 1 or 2 per cent., which renders this method less accurate than the first, which will even indicate a thousandth.

The following short table shows what per-centage each division of the burette employed to produce the turbidness in the liquid is equal to:—

48 divisions = 100·00 per cent. iodide.			
47	...	97·91	...
46	...	95·83	...
45	...	93·75	...
44	...	91·66	...
43	...	89·58	...
42	...	87·50	...
41	...	85·41	...
40	...	83·33	...
39	...	81·25	...
38	...	77·16	...
37	...	77·08	...
36	...	75·00	...

On the Preparation of Caustic Baryta. By Dr. E. RIEGEL.

The reduction of the carbonate of baryta with one-tenth charcoal and some tragacanth-mucilage, yields a baryta which constantly contains some charcoal, and most frequently also undecomposed carbonate of baryta. It may be obtained more pure by heating to redness the nitrate in a porcelain crucible; but then the heat must be long applied, which renders the preparation rather expensive. According to Vogel, a fourth part in weight of concentrated solution of caustic potash is added to a boiling concentrated solution of sulphuret of barium, when the hydrate separates on cooling in crystals, which may be purified by recrystallization. Hydrate of baryta may be obtained quicker, but less pure, by decomposing a solution of sulphuret of barium with oxide of copper; the ley generally contains a slight trace of copper.

A very simple and cheap method consists in heating a concentrated solution of sulphuret of barium with a sufficient quantity of peroxide of manganese, until reagents indicate no sulphuretted hydrogen in the liquid, and then filtering as quickly as possible. On the cooling of the hot concentrated solution, the hydrate of baryta separates in colourless, transparent, four-sided, and flattened six-sided columns, with four terminal surfaces, and the filtered ley may be used as barytic water. The author could not observe the formation of any hyposulphite of baryta. On adding a few drops of basic acetate of lead to the solution of sulphuret of barium, which had been heated with sufficient peroxide of manganese, a beautiful brick-red precipitate was formed, which however was not examined, and in subsequent experiments could not be again obtained.—*Jahrb. für Prakt. Chem.*, xii. p. 105.

Purification of Hippuric Acid. By Dr. A. BENSCH.

The fresh urine of the horse, that passed in the morning being best, is evaporated in a water-bath to one-eighth of its volume, precipitated when cold with muriatic acid, the hippuric acid collected on a strainer, strongly pressed, and treated with 10 times its weight of boiling water and excess of milk of lime. The mixture is strained, pressed, and the fluid treated with solution of alum until the alkaline reaction has disappeared; it is then allowed to cool to 104° F., and solution of bicarbonate of soda added as long as a precipitate ensues, strained and pressed, and the clear fluid precipitated with muriatic acid. The precipitated hippuric acid, after having been washed and pressed, is dissolved in boiling water, an ounce of animal charcoal added to each pound of moist hippuric acid, the boiling liquid filtered through paper, and perfectly white hippuric acid is thus obtained. The precipitates produced are readily separable from the liquid by a linen cloth, not passing through the latter when pressed; hence the purification may be accomplished in a few hours, provided the temperature, when the bicarbonate of soda is added, does not exceed 104° F.—Liebig's *Annalen*, lviii. p. 267.

On the Preparation of the Golden Sulphuret of Antimony.
By Dr. RIEGEL.

Heusler heated a mixture of equal parts dry sulphate of soda and black sulphuret of antimony with one-fourth part charcoal powder until the mass fused quietly, in which state it was kept for half an hour. The salt obtained by exhausting the fused residue was dissolved in water and precipitated with dilute sulphuric acid; but instead of golden sulphuret he obtained a kermes-like precipitate, the cause of which he ascribes to some sulphur having escaped during the operation of melting. The author repeated the experiment exactly as described, with this exception, that he employed the strongest heat for half an hour. On lixiviation and crystallization colourless crystals were obtained, which dissolved in much water, and on treatment with dilute acid yielded a beautiful orange precipitate of golden sulphuret, which however approached after drying the colour of kermes. The same result was obtained on employing less heat in melting, but then the product was somewhat less. The golden sulphuret however always exhibited, according to the author, the same composition, and a similar behaviour towards different reagents. The author recommends Schlippe's process, according to which 8 parts dry sulphate of soda, 4 sulphuret of antimony and 2 charcoal are fused together, and the extract boiled with 1 part sulphur; that according to which 6 parts carbonate of soda, $3\frac{1}{2}$ sulphur, 6 sulphuret of antimony, and $\frac{6}{8}$ part charcoal powder are fused together is not so good. More profitable is Mitscherlich's process, according to which 11 parts sulphuret of antimony, 13 parts crystallized carbonate of soda, 1 flowers of sulphur, 5 burnt and slaked lime, are digested in the cold for 24 hours with 20 parts water, and allowed to crystallize. The most simple plan of obtaining Schlippe's salt is by dissolving sulphuret of antimony and sulphur in concentrated solution of caustic soda, when, if sufficiently concentrated, a portion of the salt separates on cooling.

Of the other processes that of Trommsdorff is perhaps the best, according to which 2 parts sulphuret of antimony, 3 of sulphur and 6 of purified potash are fused together, lixiviated with boiling water, and treated with dilute sulphuric acid. Bucholz's method of preparing it is similar; he fuses 3 parts sulphuret of antimony, 8 of sulphuret of potash, and $1\frac{1}{2}$ charcoal, exhausting the mass after the addition of 1 part sulphur, and precipitating the solution with dilute sulphuric acid. Abesser's process yields a considerable product, but the colour of the preparation is not good; he recommends boiling a mixture of equal parts sulphuret of antimony and sulphur with 2 parts hydrate of lime and 8 of water, and precipitating the clear solution with pure muriatic acid. Dumesnil's method, according to which 1 part sulphate of potash, 2 of sulphuret of antimony, 1 of sulphur and $1\frac{1}{2}$ of charcoal are fused together, offers no advantages.—*Jahrb. für Prakt. Pharm.*, xii. p. 171.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Analysis of some Australian Copper Ores.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Middlesex Hospital.

MY DEAR SIR,—Considerable interest having been excited lately upon the subject of Australian mines, I beg to send you, for insertion in your Journal, the results of the analysis of a few copper ores which were submitted to me by The Australian Mining Company. The large tract of country belonging to The Australian Mining Company, from whence these ores were brought, is situated about 30 miles to the eastward of Adelaide in South Australia, and about 10 miles from the river Murray. The ores which have as yet reached this country are represented to be merely *surface* ores, and their outward appearance, as well as their chemical composition, evinces clearly enough that they must have been exposed to the influence of the atmosphere for a considerable period. Although but little or no scientific interest can be attached to the analysis of ores so changed by atmospheric influence, yet the large amount of copper which is yielded by the bulk of the ore may perhaps be thought worthy of attention by those engaged in mining pursuits; for if portions of surface ores will yield so large a percentage, what may not be expected from that which is still concealed, and has not suffered by exposure to the atmosphere?

A great portion of the ore consists of a dark brown heavy rock, through which is disseminated copper pyrites. The analysis showed it to contain—

Sulphuret of copper	38.21	} = 38.8 p. c. copper.
Oxide of copper	15.22	
Oxide of iron, with traces of alumina ..	35.96	
Insoluble matter, consisting of silica ..	0.81	
Water	6.73	
Carbonate of lime	3.07	
	100.00	

The largest quantity of ore yet imported consists of a siliceous rock, thickly interspersed with the blue and green carbonate of copper. A specimen selected, in which the blue mineral predominated, was found to consist of—

Oxide of copper with a trace of sulphuret ..	41.80	} = 33.36 p. c. copper.
Oxide of iron	2.50	
Water and carbonic acid	13.90	
Insoluble matter, consisting of silica } and a trace of sulphate of lime .. }	42.23	
	100.43	

A specimen of the same ore, in which the green carbonate was in greater quantity, gave—

Oxide of copper	17.57 = 13.567 p. c. copper.
Oxide of iron	3.28
Water and carbonic acid	6.89
Insoluble matter, consisting of silica } with a trace of sulphate of lime .. }	73.20
	100.94

A specimen, bearing every resemblance to copper pyrites, gave—

Sulphuret of copper	40.525 = 32.29 p. c. copper.
Sulphuret of iron	19.638
Oxide of iron	35.026
Insoluble silica	4.800
Water and carbonic acid	4.210
Loss	1.801
	100.000

A specimen, in which sulphuret of copper was disseminated through a dark brown rock, much of which from exposure to the atmosphere had become ochreous, and was interspersed with carbonate of copper, gave—

Sulphuret of copper	26.65 = 21.24 p. c. copper.
Sulphuret of iron	7.29
Oxide of iron	35.28
Water and carbonic acid	12.36
Insoluble silica	18.42
	100.00

The last specimen that was analysed was ochreous, with veins of iron glance and much carbonate of copper:—

Oxide of copper	22.97 = 18.33 p. c. copper.
Oxide of iron	18.14
Insoluble silica	49.50
Water and carbonic acid	9.39
	100.00

The foregoing analyses cannot be strictly called assays; the object desired by the Company, and for which the analyses were undertaken, being to ascertain of what the ores were composed, and what per-centage of copper was contained in the minerals forming the chief bulk of each specimen of ore.

I remain, my dear Sir,

Yours very truly,

EDM. RONALDS.

How to colour German Silver blue. By R. BÖTTGER.

When a bright, polished, perfectly clean plate of German silver, of about 3 to 4 square inches surface, is placed in a shallow glass dish, then touched at any point with a bar of zinc, and covered for 3 or 4 lines with a tolerably concentrated recently prepared mixture of pure ferridcyanide of potassium and pure perchloride of iron dissolved in water, the electro-negative German silver is seen in a few instants to become enveloped in a thin splendid blue coating, which will not resist, it is true, any strong friction; but adheres however so firmly that it cannot be removed by mere rubbing with the hand.—*Chem. und Phys. Vers.*, p. 44.

THE CHEMICAL GAZETTE.

No. XCIX.—December 1, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a new Acid of Sulphur. By H. WACKENRODER.

WHEN crude muriatic acid, which has been treated with sulphuretted hydrogen in order to remove any arsenic, and then exposed for some time, is rectified, sulphurous acid is disengaged, and minute flakes of sulphur separate in the distillate, especially when the muriatic acid still contains some sulphuretted hydrogen, so that the first portions which pass over are rendered turbid, and contain sulphuric acid. This phenomenon can only be explained by supposing that the sulphurous acid contained in the crude muriatic acid was not completely decomposed by the sulphuretted hydrogen. Something similar occurs when milk of sulphur has been precipitated from a solution of sulphuret of potassium by just a sufficient quantity of sulphuric acid. In this case the clear filtered liquid, which smells strongly of sulphuretted hydrogen, soon becomes turbid from the decomposition of the hyposulphurous acid, and acquires the odour of sulphurous acid. If the decomposition of the hyposulphurous acid and of the sulphuretted hydrogen were complete, 3 equivs. S should be reduced from every 1 equiv. of the two acids, while the quantity of the eliminated sulphur is far smaller. The author therefore undertook a more minute examination into the behaviour of sulphuretted hydrogen towards sulphurous acid.

When a current of sulphuretted hydrogen is passed into a saturated aqueous solution of sulphurous acid at a mean temperature, decomposition soon ensues, and continues until the sulphuretted hydrogen is predominant, while a small quantity of sulphur separates. Collected on a filter it dries very slowly, and then forms a greenish-yellow shining varnish upon the paper. After 8 days at 68° F. it becomes hard and brittle, and resembles ordinary sulphur. With a magnifying power of 200, crystalline granules, but without any distinct faces, may be detected in the deposit, which when dry is volatilized without any residue, and without giving off any sulphuretted hydrogen.

When a current of sulphuretted hydrogen is passed into aqueous sulphurous acid, a new acid is formed, which the author calls pentathionic acid. The liquid saturated with sulphuretted hydrogen passes turbid through the filter, which however can be avoided by

mixing with it a neutral alkaline salt, for instance chloride of sodium or copper turnings which have been slightly heated in the air. The small quantity of oxide of copper which the liquid takes up in this operation can be removed by a little sulphuretted hydrogen, and this again by warming. When the acid is to serve for the preparation of the barytic salt, the oxide of copper need not first be removed, for it is completely separated by shaking the acid liquid with carbonate of baryta and some barytic water. The pure acid liquid is colourless and void of odour, has an acid and at the same time bitter taste, and is not altered by long keeping. It can be concentrated at a gentle heat to 1.370 spec. grav.; it then deposits, if the temperature is very low, some acicular crystals. The concentrated acid altered very little in the course of half a year, and only deposited a few flakes of sulphur. When the concentrated liquid is heated further in a retort, sulphuretted hydrogen gas first escapes, and then sulphurous acid along with water; on which account sulphur likewise separates in the distillate, just as is the case when the crude muriatic acid, which has been treated with sulphuretted hydrogen and is contaminated with sulphurous acid, is rectified. There is left in the retort the hydrate of sulphuric acid, upon which brownish-yellow drops of sulphur float. The dilute acid yields with the alkalies and alkaline earths perfectly neutral solutions; but the salts, with the exception perhaps of the lead salt, cannot be obtained in a solid state.

To ascertain the composition of the acid, it was prepared with the assistance of metallic copper, neutralized accurately with carbonate of baryta, without the application of any heat, and then divided into two weighed portions. One portion was decomposed with dilute sulphuric acid, when 3.621 per cent. of sulphate of baryta were obtained; the other portion was treated with an excess of chlorine gas, when, besides 3.305 per cent. sulphate of baryta, 0.313 per cent. sulphur = 2.267 sulphate of baryta, separated. From the liquid treated with chlorine there was moreover obtained with nitrate of baryta 9.448 per cent. pure sulphate of baryta; consequently the saline solution yielded in the second case 4.148 times as much baryta as in the first, or leaving out of consideration the quantity of sulphate of baryta first precipitated by the chlorine, the sulphate of baryta in the second case amounts to exactly 3 times as much as in the first; and when the sulphate of baryta formed by the chlorine is taken into consideration, 3.5 times as much; consequently the new acid must contain either 4 equivs. or $4\frac{1}{2}$ equivs. sulphur to 1 equiv. base. In another experiment, an acid was examined which had been prepared from aqueous sulphurous acid and sulphuretted hydrogen, shaken with slightly oxidized copper turnings, filtered, and neutralized with carbonate and some caustic baryta. The first portion of the saline solution yielded, on precipitation with sulphuric acid, 0.781 pure sulphate of baryta; the other portion was mixed with solid caustic potash, containing no sulphuric acid, and evaporated to dryness. The residue was heated with nitric acid, evaporated, and again dissolved in water; some chloride of

barium was now added to the liquid ; the quantity of pure sulphate of baryta thus obtained amounted to 4.078 per cent. of the saline solution ; consequently the two quantities of sulphate of baryta are as 1 : 523. On repeating the experiment, almost the exact proportion of 1 : 5 was found. The number of atoms of oxygen which form the new acid with the 5 atoms of sulphur could not yet be ascertained by experiment ; it is, however, probable that the composition of the acid is $S^5 O^5$.

Pentathionic acid is characterized by the following properties : it is not altered by sulphuretted hydrogen ; even after months' keeping, but an exceedingly slight turbidness was perceptible. Dilute sulphuric or muriatic acid produces no turbidness, but the hydrate of sulphuric acid precipitates sulphur, and entirely decomposes the pentathionic acid. Concentrated nitric acid is decomposed with the acid, forming sulphuric acid, and with the elimination of sulphur ; the same is the case with chlorine gas. Chloride of barium does not cause any turbidness when the acid is free from sulphuric acid ; perchloride of mercury gradually produces a white or whitish-yellow precipitate, which is white and flocculent even after several days. A white turbidness is immediately produced, with a large excess of perchloride of mercury. The percyanide of mercury gradually gives rise to a whitish-yellow or lemon-coloured precipitate, which only blackens after long keeping. In the solution of pentathionate of baryta a red or yellow precipitate is obtained, when some nitric or oxalic acid has been previously added. Pernitrate of mercury yields, when either the pentathionic acid or the precipitant is in excess, a voluminous white precipitate ; the protonitrate produces, both in the recently prepared pentathionic acid as well as in that which has been preserved for some time, immediately a copious flocculent precipitate of a dark yellow or lemon-yellow colour ; this precipitate very slowly becomes black in the sun. With a strong excess of the reagent, it acquires a yellowish-white or white colour without being further changed. When tetrathionic, trithionic or dithionic acid are mixed with it, a black precipitate is first formed, and only after a larger addition of the reagent the yellow precipitate of the protopentathionate of mercury. The pernitrate of mercury slowly yields a yellow precipitate, which soon becomes brown, then black, and finally acquires a metallic lustre. Acetate of lead produces no precipitate ; but with a solution of the barytes salt yields a copious white deposit, which is soluble in acetate of lead ; sulphate of copper causes no perceptible change ; protochloride of tin yields a white flocculent precipitate, which becomes somewhat yellowish on long standing ; when some ammonia is added at the same time, a chocolate-brown precipitate is formed, probably the protosulphuret of tin. Perchloride of iron colours the acid pale yellow, and a blue precipitate is formed on the addition of ferrideyanide of potassium, only after a considerable interval. Sulphur does not dissolve in pentathionic acid, although the sulphur set free at its formation is very tenaciously held in suspension. Phosphorus does not act upon the acid at a moderate heat. When copper filings are boiled with acid

of 1.032 spec. grav., sulphurous acid escapes, sulphuret of copper is deposited, and the liquid contains sulphuric acid. On boiling with metallic iron, sulphuretted hydrogen is first given off, then sulphurous acid, and in the retort is left sulphuret of iron, along with the sulphate and hyposulphite of the protoxide of iron. On evaporating pentathionate of baryta, a yellowish-white crystalline powder separates, and the liquid contains hyposulphite of baryta. When the powder is heated, the sulphur is burnt, and a lemon-coloured powder, which is insoluble in acids and not decolorized by fusion with chlorate of potash, is left; but on boiling it with nitromuriatic acid, sulphate of baryta, free from sulphuric acid and sulphur, is obtained. When the still turbid pentathionic acid is saturated in the cold with carbonate of soda, the whole of the suspended sulphur is deposited; on heating the clear filtered solution to boiling, it becomes yellow, diffuses a disagreeable odour, and deposits tenacious greenish-yellow flakes. After filtration it again becomes somewhat turbid, but continues neutral; on further evaporation it yields on cooling large crystals, which proved, both from their properties as well as their composition, to be pure hyposulphite of soda; their analysis yielded—

Soda	25.678	1 =	25.128
Sulphur	26.288	2	25.863
Oxygen	10.334	2	12.865
Water	37.700	5	36.153

On the further concentration of the mother-ley crystals of the sulphate of soda were obtained.

Nothing positive can be stated as to the origin of pentathionic acid; but we may admit preliminarily that 5 atoms SO^2 and 5 atoms HS are mutually decomposed to form 1 atom S^5O^5 and 5 atoms HO, with elimination of 5 atoms S. But the above acid might likewise be tetrathionic acid in combination with sulphuretted hydrogen, $5\text{SO}^2 + 6\text{HS} = 5\text{HO} + 6\text{S} + (\text{S}^4\text{O}^5 + \text{HS})$. This view explains a peculiar reaction of the barytic salt better than the preceding. When, for instance, the neutral solution of the barytic salt is heated, it becomes coloured, but remains neutral, and then yields with nitrate of silver a black precipitate, and no longer a yellow one. It remains clear and unaltered on the addition of hydrocyanic or muriatic acid; but when sulphuretted hydrogen is added, it is not only immediately rendered turbid by reduced sulphur, but acquires at the same time a strong acid reaction. On adding sulphuretted hydrogen to the pure acid, no turbidness arises; but on the addition of baryta, sulphur is immediately precipitated. The decomposition of the barytic salt by sulphuretted hydrogen is not obviated by the previous addition of hydrocyanic acid; an addition of hydrochloric acid, on the contrary, prevents it entirely.—*Archiv der Pharm.*, xlvii. p. 272.

On the Composition of Fibrine. By Prof. SCHLOSSBERGER.

Mulder, in his analysis of fibrine, repeatedly obtained never more than 15.7 per cent. of nitrogen; Dumas and Cahours, on the con-

trary, in their numerous recent analyses of the fibrine of the blood of man and various animals, always found about 1 per cent. more nitrogen. The author analysed some fibrine, prepared by Mulder himself from ox-blood, and freed most carefully from fat; he obtained 52.42 per cent. carbon, 6.92 per cent. hydrogen and 15.51 per cent. nitrogen. The ash amounted to 1.11 per cent.—Liebig's *Annalen*, lviii. p. 95.

On the Presence of Sulphuret of Arsenic in Shell-lac.
By W. BUCHNER.

Shell-lac, or lac in plates, is well known as an article of commerce. Grain-lac is produced from the shell-lac. When the *Coccus lacca* has punctured the young branches of different plants, especially *Aleurites laccifera*, Wild, *Croton aromaticus*, *Butea frondosa*, and *Zizyphus jujuba*, which grow in the East Indies, a juice flows from the wound. The female insects adhere to the wounded place, become moistened, and finally enveloped by the fluid, which thus incloses it in a cell; subsequently the young larva creeps out of this, the dead body of the mother remaining inclosed. Whilst the sap is enveloping the insect, a red colouring matter, similar to cochineal, is imparted to it by the latter, which may be separated by ebullition with water and precipitation with alum or some aluminous compound, and is known in commerce as lac-dye. If the sap is allowed to dry upon the branches, and then brought into commerce with the fine twigs, it forms stick-lac. When removed from the twigs it forms grain-lac. When collected previously to its drying, and whilst still moist, fused, strained and spread out, it forms shell-lac, or lac in plates. The colour of shell-lac varies, being either orange, pale yellow, brown, liver-coloured, reddish-brown or black. The difference of colour depends upon the plants, the place where they grow, whether it has been obtained from them before or not, and the success of the fusion.

The various kinds of lac do not essentially differ in chemical composition. The amount of colouring matter varies according to the kind; orange shell-lac contains the least, grain-lac the most. Grain-lac contains most animal remains, fragments of wood and earthy constituents; the varieties of shell-lac do not differ essentially from each other in these particulars. Shell-lac undoubtedly contains wax; the quantity amounts to 3 per cent. It resembles Japan vegetable wax; is hard, brittle, whitish-yellow, of a peculiar odour, difficult to bleach, and takes an excellent polish.

Those portions which in the analyses of lac are called *earthy*, consist apparently of fragments of wood, insect-remains, grains of quartz, and various grains of sand from all kinds of stones, in fact the common constituents of drift-sand. The most remarkable components of it consist of a mass of yellow grains, varying in size from the smallest particle to the size of a lentil. At first I considered them to consist of sulphur, but on analysis I found them composed of sulphuret of arsenic. A body the size of a lentil could not have

got into the lac from absorption by the plant; it must have arrived there mechanically. The amount of the sulphuret of arsenic varies, being entirely dependent upon the quantity of sandy residue; it occurs in every kind. It amounted to about one-eighth of the sandy residue. The fact of the occurrence of this sulphuret of arsenic in the grain-lac shows that it is not mixed with lac by artificial means, because this comes to us in a natural state, unaltered by any manufacturing processes. The grain-lac contains a much larger amount of the remains of insects, particles of wood and coarse sand, consequently of sulphuret of arsenic, than shell-lac. Hence we cannot entertain a view of the intentional admixture of sand and sulphuret of arsenic. It is more than probable that the sandy particles and the sulphuret of arsenic they contain, are derived from the drift-sand, which, urged by wind, is driven against the trees from which the lac exudes; the surface of the latter, being moist, readily retains these particles.

Grain-lac, as found in commerce, cannot be fused, poured into leaves and extended whilst warm, as is done in the East Indies. The fusing-point of the resin is too near its decomposing point; hence abroad it must exist in some other state than with us. At the time of its flowing from the wounded tree it must be more fluid. This fluidity arises from the water it contains, which forms with the resin a kind of emulsion. Shell-lac is capable of combining with a very large quantity of water; I found 120 parts *combined* with 20 parts; it then forms a hard substance, which can only be softened by heat. Probably in making shell-lac the grain-lac is collected in a semifluid state, and the sap which is to form grain-lac is allowed to dry upon the tree; most probably a mass of drift-sand, &c. adheres to the lac whilst in this viscid state.

The author concludes his paper by stating his belief that yellow fever is produced by the action of the sulphuret of arsenic which exists in the drift-sand, and is wafted with the latter by the wind. His views however appear to us far too visionary and too little based upon facts to induce us to append them.—*Annal. der Pharm.*, lix. p. 96.

On the Products of Decomposition of the Protoxalate of Iron at a high Temperature. By C. RAMMELSBERG.

According to Magnus, the residue, on igniting protoxalate of iron in a closed vessel, consists of metallic iron possessing pyrophoric properties. According to Döbereiner, it consists of peroxide of iron, protoxide and carburet of iron. According to the latter and the author, the protoxalate of iron is $\text{FeO}, \text{C}^2\text{O}^3 + 2\text{HO}$, and its composition 40·03 per cent. FeO , 39·98 C^2O^3 , and 19·99 HO . The salt, dried at 248°F ., was slowly heated in a small retort to redness. The black residue amounted to 41·83 per cent. [Döbereiner obtained 38·8–39·4.] It could therefore not be metallic iron. On burning it in a current of oxygen, 100 parts of the salt yielded 44·31 peroxide of iron, and 0·029 per cent. carbonic acid = 0·008

carbon; so that it must have consisted of 41.83 iron and oxygen + 0.03 carbon. Now since the salt contains 31.15 per cent. iron, 100 parts of the residue, after deducting the carbon, must contain 75.06 per cent. iron and 24.94 oxygen, which correspond to a combination of Fe^6O_7 , or $4\text{FeO} + \text{Fe}^2\text{O}_3$. 100 parts of this compound should yield on burning 107.14 Fe^2O_3 ; experiment gave 106.77. The disengaged gases must consist of about 5 vols. carbonic oxide and 4 vols. carbonic acid.—Poggendorff's *Annalen*, lxviii. p. 276.

Determination of the Quantity of Sulphur contained in Ox-bile; with Remarks on the Mutual Relations which subsist between that Body, Taurine, Cystine and Lithofellic Acid. By GEO. KEMP, M.D. Cantab., F.C.P.S.

Few subjects have attracted more attention or secured more diligent study and elaborate research, for some years, than the composition of the ox-bile, the nature of the changes effected by artificial agents, and the mode by which its influence becomes displayed in the phenomena of digestion. It is with more than ordinary pleasure that, on reviewing the labours of others, the writer finds them not only confirmatory of his original analyses, as printed in several periodicals during 1843 and subsequent years, but, as he conceives, placing the composition of the fluid in question beyond all reasonable doubt. Hitherto however a slight difficulty remained in forming a rational formula for its composition, in consequence of the presence of a portion of sulphur, apparently indeed very small, but still likely to affect the accuracy of subsequent deductions. Having now determined the amount of the element alluded to, we are evidently in a condition to place the whole research amongst established facts, and apply our knowledge to the determination of the nature of phenomena which have hitherto been involved in much obscurity.

In the year 1843 the writer published the following fact in Erdmann's 'Journal:—“When the ash (of the bile) was neutralized with acetic acid, previously to determining the quantity of chloride of sodium by means of the acetate of silver, a distinct smell of sulphuretted hydrogen was perceived. Paper moistened with a solution of a lead salt was blackened.” The extent of the research has deferred the necessary determination of the quantity of sulphur up to the present time. It is well known, to all who have been engaged in the analysis of the bile, that great precaution is necessary, when burning it in a crucible, to determine the amount of inorganic matter; and the difficulty is much increased when it is mixed with oxidizing agents for the determination of the sulphur. The following analyses were differently arranged:—

I. 354 milligrammes of the ox-bile, treated as so often described, were carefully mixed with chlorate of potash and carbonate of potash, the mixture introduced into a large platinum crucible, and exposed to the heat of a spirit-lamp. The action was very violent; but, by inclining the crucible and placing the cover on, but little

loss occurred. The result, dissolved in distilled water and treated with nitric acid in excess, was now tested for sulphates, and the sulphur estimated in the form of sulphate of barytes, which amounted to 78 milligrammes.

II. 300 milligrammes of bile were mixed as above, the mixture introduced into a long sealed tube of Bohemian glass, and thus exposed to the action of a spirit-lamp. The oxidation completed, the contents were dissolved, nitric acid added in excess, and the sulphur estimated as above, the amount of sulphate of barytes being 68 milligrammes. Reducing to 100 parts, and eliminating the sulphur—

I. contains 3.0 per cent. of sulphur.

II. ... 3.1

We now proceed to consider the influence of these facts upon the formula for the ox-bile.

The results of the ultimate analysis, in the normal condition of the body, as a soda salt are as follows:—

Carbon	59.90
Hydrogen	8.90
Nitrogen	3.40
Oxygen	17.63
Sulphur*	3.10
Oxide of sodium	6.53
Chloride of sodium	0.54
	100.00

The equivalent number therefore for the soda salt is 5980, leading to the formula $C^{28}H^{43}NO^{11}S + NaO$.

In the year 1841 an analysis of lithofellic acid was made by MM. Ettling and Will†; at the conclusion of their report they express a conviction that its constitution must bear a certain relation to the bile, and that the ultimate analysis of that body, when completed and compared with their analyses of lithofellic acid, would decide the formula. On examining the subject, however, it will be found involved in some difficulty; partly from the difference of the formulæ proposed by MM. Ettling and Will and Prof. Wöhler, partly from the great discrepancy in the data furnished. Thus, the former authorities deduce the formula $C^{42}H^{38}O^8$ for the hydrate of the acid in question; Prof. Wöhler, $C^{40}H^{36}O^8$ ‡. Again, the equivalent number, as found from the silver salt, for the hydrate is 4388; that from the lead salt 1451§, or pretty nearly one-third of the

* The calculation requires 3.3.

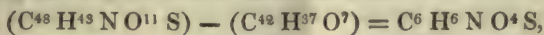
† Liebig's Annalen, vol. xxxix. p. 242.

‡ Liebig's Annalen, vol. xli. p. 150. The equivalent however from this formula is 4250, or as nearly as possible the same as Ettling and Will found for the *anhydrous* acid. The formula, as proposed by these last authorities, although involving too high an atomic weight for the hydrate, agrees better with the data.

§ With reference to the lead salt, the writer would remark, as a matter of caution to the student, that in electro-negative bodies of this nature the equivalent number should never be made to depend on the lead salt, unless confirmed by a silver or barytes salt—the former if possible. In the bile particularly the mode of

former; whilst that from the soda salt, as found by Prof. Göbel, bears no relation to either, being 3863. Not to occupy too much space, the writer begs to refer those interested in the subject to the papers quoted, and proceeds to suggest an explanation, which, if correct, is another interesting case of mutual compensative function between the liver and kidneys, and may prove a source of important clinical inquiry into the consentaneous formation of cystine in the urinary and lithofellic acid in the biliary organs.

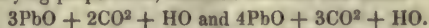
Deducting the first formula of the anhydrous acid from the formula proposed for the bilic acid, we have left



differing from cystine in containing 1 equiv. less of sulphur. If the writer's originally-proposed number of hydrogen equivalents be correct, viz. 42, it differs from cystine by an equivalent of sulphuretted hydrogen. It is also pretty apparent that some relation exists between taurine and cystine; that the former is, in fact, the result of the oxidation of the other; for, by adding 1 equiv. of water and 5 of oxygen to cystine, we have left the formula of taurine plus 2 equivs. of carbonic acid, $C^6 H^7 N O^{10} S^2 = C^4 H^7 N O^6 S^2 + CO^2$. The analysis of the lithofellate of the oxide of silver is necessary to decide the point.

During the last year a most important addition to our physiological knowledge of the bile has been made by the well-directed experiments of Prof. Redtenbacher* on the influence of oxidizing agents on that fluid; and the deductions made by the writer of this paper, in the year 1844, on the volatile fatty acids, as caproic and butyric acids, being the results of oxidation, either directly, by the appropriation of oxygen, or relatively, by the addition of bodies containing a larger proportion of that element, proved to be correctly devised. Another interesting fact has also been developed by the Professor—the production of *valerianic acid* by similar means. Some weeks since, and quite independent of this research, on forming valerianic acid from the oxidation of indigo, a smell was observed precisely similar to that occurring during the analysis of ox-

precipitation directed by Liebig is quite inadmissible, as uniform results cannot be obtained. The writer has made between 20 and 30 attempts to make it answer at Giessen, Cambridge, and on this island, with results as follows:—Oxide of lead, 21, 27, 32, 36, 40 and 42 per cent.; and, on examining into the causes of this discrepancy they appear to be mainly three:—1st, that pointed out by Berzelius, in his work as translated by Wöhler, vol. vi. p. 34; 2nd, there are two, if not more, well-defined lead salts of bilic acid, which are precipitated in various proportions, according to temperature and other circumstances; 3rd, this precipitate seems, in many points, to resemble that produced during the manufacture of white lead, which, according to the well-known researches of Mulder, Richardson and Payen, is not a neutral carbonate, but a mixture of oxide of lead, carbonic acid and water, in varying proportions, included between the limits



The mode adopted by the writer for obtaining the neutral and basic lead salts of the bile, is too lengthy to be described in a note.

* Chem. Gaz., 1846, p. 269.

bile for nitrogen by Will's method; and this led to a comparison of the composition of this fluid and the above acid.

If we construct an empirical expression for valerianic acid, involving the same number of equivalents of carbon as in ox-bile, we find it becomes $C^{43} H^{43} O^{14}$; now, by means of oxidizing agents on the ox-gall, we may safely conclude, from analogy, that the sulphur is oxidized independently of the other portions; and, by the addition of 3 equivs. of water to the residue, the formula proposed for ox-bile becomes $C^{43} H^{46} N O^{14}$, or $C^{43} H^{43} O^{14} + NH^3$, or valerianic acid and ammonia. The whole molecular constitution of the bile is of course broken up, as the rational formula for valerianic acid is $C^{10} H^9 O^3$.

The number of equivalents for hydrogen still remains uncertain, but must evidently be 42 or 43; at present the mode for determining the quantity of that element in a given organic body is very defective; but a method which will shortly be published bids fair to remove the difficulty.

St. John's, Isle of Man, Nov. 17th, 1846.

On the Oil of Monarda (Horse-Mint). By A. E. ARPPE.

The oil of *Monarda punctata*, which is officinal in the United States, separates readily into an elæoptene and stearoptene. The first forms a yellowish-red fluid, which possesses the odour of thyme, and passes over when distilled with water of a bright yellow colour. The oil, thus purified and freed from water, boils at $435^{\circ} F.$, when it becomes of a darker colour. As it cannot be assumed that this oil, the boiling-point of which approaches so closely to that of the stearoptene, was obtained perfectly free from the latter, no safe conclusion as to its composition can be expected from the analysis, which yielded 86.41 per cent. C, 9.85 H, and 3.74 O. Exposed to the air, or placed in contact with substances containing much oxygen, it very easily changes to a resin, becoming brown and thick, and exhibits on analysis a considerable decrease in the amount of carbon.

The stearoptene forms large crystalline fragments, which are coloured yellowish by the adherent fluid oil, and the odour of which has a striking resemblance to that of thyme. It can be obtained perfectly colourless by pressure between blotting-paper, and quite pure by distillation either alone or with water. When submitted alone to distillation, the product solidifies in the recipient immediately, and forms very distinct crystals of remarkable lustre, which retain the above-mentioned odour and have an acrid burning taste. It leaves on distillation a small quantity of a brown resinous mass, which is soluble in alcohol. When the crystals thus obtained are distilled with water, they melt to an oil, and appear to undergo some change, as during ebullition the oil floating on the water becomes brownish; however, it distils over entirely, and the residuary water, which is wholly destitute of smell, has only a faint brownish tint. The distillate floats as a colourless oil on the water, and exhibits the

remarkable property of retaining its fluid state for a very long time; but congeals, on being touched with a hard body, immediately at the point of contact, and extending rapidly over the entire surface of the oil. The greater portion forms large regular crystalline plates, but a few drops change into small spherical tufts. The crystals or spheres thus produced are distinguished by their opacity and their decomposed appearance from those obtained by the distillation of the stearoptene alone. To render them transparent and lustrous, it is only requisite to melt them and allow them to solidify; but if melted frequently, the stearoptene passes into the non-crystalline state, without its being possible to state more precisely what conditions give rise to this peculiar behaviour. When the fluid stearoptene is touched with a hard body, the formation of crystals begins again, and the crystals are for the most part opaque; but in general it must have remained for some time in its fluid state before it can be thus brought to solidify. The stearoptene melts at 119° , and solidifies at 101° ; when heated to 158° , it solidifies at 93° , when the thermometer rises again to 101° ; heated to 221° , it congeals at 92° , upon which the thermometer ascends to 99° ; heated to 284° , it solidifies at 88° , and the thermometer subsequently ascends to 96° ; lastly, when heated to 338° , it solidifies at 81° , and the thermometer ascends to 95° . Its boiling-point is 428° .

These numbers show that the point of solidification descends as the heating-point rises, and that the liberated heat amounts up to 275° only to 7° , but at 338° it is already 14° . At this temperature, when more caloric is set free, its tension is greater and its escape easier, which facilitates crystallization; to which is likewise owing the circumstance, that the stearoptene, when distilled alone and consequently heated to 428° , cannot persist in the fluid modification; on the contrary, when distilled with water, all the conditions requisite to its production are given.

The stearoptene is very easily soluble in æther, and especially in alcohol, and separates in crystals from both solutions on spontaneous evaporation. The substance was purified for analysis by three distillations, and the combustion made in a current of oxygen. The author found—

Carbon	79.77	79.88	80.00	10	80.00
Hydrogen	9.25	9.50	9.52	7	9.33
Oxygen	10.98	10.62	10.48	1	10.67

If we regard this stearoptene as an oxide $= C^{10}H^7 + O$, we find such a relation between its composition and that of the elæoptene from which it separated, that we may assume in the elæoptene 3 atoms of the same radical combined with 1 atom of oxygen $= 3C^{10}H^7 + O$, with which the per-centage composition found agrees tolerably well.

When dry muriatic gas is passed over the solid stearoptene, it very quickly becomes brown, and after removal of the excess of acid purple-coloured. The effect is the same whether the mass be warmed or heated to boiling; on cooling it separates in dark purple

crystals, which however consist for the greater part of unaltered stearoptene, as was to be expected, since the total increase in weight did not amount to more than 2 to 3 per cent. On distilling the coloured crystals in a small retort, the stearoptene first passes over quite colourless, but the red compound likewise distils over unaltered. Caustic alkali turns the red colour to blue, and on the application of heat into emerald-green, both which colours gradually return to red on exposure to the air. The red mass yields a beautiful blue solution with hydrate of barytes. When carbonic acid is passed into this, the baryta is precipitated, and at the same time the colouring substance, which imparts a blue colour to the precipitate, which colour however subsequently becomes red. At last the entire precipitate is bright red and the precipitate colourless. The red colouring substance can be extracted with alcohol from the red baryta compound, and obtained in a solid state by evaporating the alcohol as a dark violet amorphous mass. It is volatilized by heat as a red gas, resembling indigo-blue, contains chlorine, and can be distilled without decomposition.—Liebig's *Annalen*, lviii. p. 41.

On the Formation of Caoutchouc as Residue of the Combustion of Drying Oils. By L. E. JONAS.

Linseed oil, exposed to a high temperature, yields a thick, more or less brownish residue, resembling turpentine, and commonly called varnish. If this residue is boiled for a long time in water rendered acid with nitric acid, taking care to replace that which is evaporated, and constantly to dilute the acid sufficiently to prevent its too violent decomposing action, a body is obtained which gradually solidifies, and which when removed from the water has a plaster-like consistence, without adhering to the fingers. During ebullition the peculiar odour of acroleine was disengaged, which ceased to be perceptible at a low temperature, and when the mass was heated alone, after having been washed in water to remove every trace of nitric acid.

This residue is not fusible by itself, and the experiment made with a view to melt it caused it to assume great elasticity and a striking resemblance to caoutchouc. Its mode of preparation imparts a more or less brownish colour to it; it adheres firmly at its surfaces of section, and is perfectly similar in consistence to the mass which is obtained by boiling ordinary caoutchouc for several days; it becomes softer by boiling in water, swells in æther containing no alcohol, and subsequently dissolves partly in it. Alcohol precipitates it from this solution, and the product thus obtained is transparent in thin layers after the evaporation of the æther which it retained. The solution of this body in sulphuret of carbon forms an emulsion; it is entirely soluble in oil of turpentine free from resin; on evaporating these solutions, it is re-obtained with its primitive properties; it swells and softens in naphtha, without dissolving in it. When boiled with a concentrated solution of caustic potash, it diminishes in volume, hardens without colouring the liquid, with-

out dividing, still less dissolving; nevertheless if the solution be diluted, it gradually dissolves in it with a brown colour, and is precipitated from it unaltered by the addition of muriatic acid. Tissues may be rendered water-proof by impregnating them with æthereal solutions of this substance, as it dries in thin layers in the air.

Walnut and poppy oil furnish, under the same circumstances, the same body as linseed oil; on account of its properties the author calls it *oil-caoutchouc*. The quantity obtained from these different oils is in exact proportion to their drying properties; thus walnut and linseed oils yield at least 8 to 10 times as much as poppy oil.

When 1 part of sulphur is dissolved in 2 parts of boiling linseed oil, and the temperature is not sufficiently lessened towards the end of the operation, frequently the entire mass is suddenly converted into a gelatinous body not very unlike *oil-caoutchouc*, and which does not dissolve entirely either in fatty or in essential oils. When this is boiled with water acidified with nitric acid, the whole amount of sulphur is gradually converted into sulphuric acid, and the inspissated oil is left in its original form, but has a tile-red colour, and may be pressed without exhibiting the properties of the elastic *caoutchouc*. Sacc also states that linseed oil is suddenly converted on boiling into a gelatinous *caoutchouc*-like mass; and that, on treatment with nitrous acid, it becomes red and tenacious, without a trace of elaidine being formed. Castor oil, heated above its boiling-point, becomes brown, and evolves irritating inflammable vapours. If during the burning a crust is observed to form at the margin of the vessel, the flame must be extinguished, as castor oil froths but very little, and otherwise the yellowish-white residuary mass would become brown and carbonized. The porous residue, insoluble in æther and essential oils, is sometimes elastic and always tasteless; boiling caustic potash dissolves it, and converts it into a soap, which on the addition of muriatic acid yields a fat acid of acrid burning taste.—*Archiv de Pharm.*, xlv. p. 159.

On the Chlorite of Proteine.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,—The last post brought me Mulder's reply to Liebig; and I must not lose time in directing your attention to my recent paper on *proteine*, where the *chlorite of proteine* is said to contain sulphur. Not having Prof. Mulder's original papers, I considered myself perfectly safe in implicitly following the directions of Berzelius (vol. ix. p. 813) for the preparation of that body; directions which are likewise transcribed into the works both of Graham and Kane, under the term *chloro-proteic acid*; no reasonable person can therefore blame me for trusting to such high authorities. It is perfectly clear, from Prof. Mulder's brochure, that the body I analysed was *not identical* with *his* *chlorite of proteine*; and that the correct mode of forming that body is first to prepare the *proteine* according to his directions, which ensures the absence of sulphur, and then to form

the chlorite by means of chlorine gas. Prof. Mulder's lucid statement will no doubt be perfectly satisfactory to every one capable of forming an opinion on this weighty subject.

I remain, Sir,

St. John's, Isle of Man,
Nov. 21, 1846.

Your very obedient Servant,
GEO. KEMP.

On the Behaviour of various Metals towards an aqueous Solution of Cyanide of Potassium. By Dr. L. ELSNER.

Although it is known that metallic gold, silver, copper and iron, dissolve at the ordinary temperature in aqueous solutions of cyanide of potassium without any cooperation of the galvanic current, the behaviour of iron alone has been accounted for by Prof. Liebig. The author therefore examined the behaviour of other metals towards solutions of cyanide of potassium, in order to arrive at a general explanation. Zinc, iron, nickel, copper, silver, cadmium, mercury, gold, platinum and tin, were employed for the experiments either in the state of thin plates or as fine filings. The cyanide of potassium was dissolved in 10 parts of water freed from air; the several metals were placed in test-tubes filled three-fourths with the solution of cyanide of potassium, then closed air-tight with cork and sealing-wax, and inverted. After several days not the least external change was perceptible in the case of gold, silver, tin, cadmium and mercury; only with leaf-gold and leaf-silver was a decrease of the metals employed to be observed. On the contrary, the copper, zinc and nickel exhibited a very distinct evolution of gas, especially the three first. Platinum was submitted to a second experiment:—A weighed piece of foil was used for 24 hours as anode in the silvering of a key; but during this time it did not in the least decrease in weight. After several days the solution of cyanide of potassium was filtered from the copper, iron, zinc and nickel, and the solution slightly acidulated with pure muriatic acid, which produced a white precipitate in all; this was filtered, and afteredulcoration examined with a blowpipe, and gave with microcosmic salt and soda the reactions of the corresponding metals. It is evident therefore that these latter are dissolved with decomposition of water (for the gas disengaged was hydrogen), oxidize a part of the potassium, and combine with the liberated cyanogen. The solutions filtered from the silver, tin, cadmium and mercury, were supersaturated as above with muriatic acid; but no precipitate was produced in the liquids which had been in contact with mercury and tin by muriatic acid or sulphuretted hydrogen; however, a small quantity of cadmium and of silver had dissolved. But since no decomposition of water had occurred in their case, the oxygen requisite to oxidize the potassium must have been derived from the superjacent stratum of air. The most considerable solution had occurred with the leaf-gold and the leaf-silver, which had been employed in very thin lamellæ, conse-

quently most oxygen must have been absorbed in their case. On immersing a burning match slowly into the stratum of air, immediately after removing the cork the flame was instantly put out. On removing the cork under water from a tube in which cyanide of potassium and silver had been in contact for eight days, the water ascended in the tube. In another tube, which contained cyanide of potassium and silver, and which was closed by mercury, a distinct ascent of the mercury was perceptible after a few days. In these cases therefore there was evidently an absorption of oxygen. When pure, porous, precipitated silver was digested in a perfectly full glass with a solution of cyanide of potassium, scarcely any opacity was produced by muriatic acid; but after filtering the contents of the flask, the filtered solution yielded with muriatic acid a distinct white precipitate, so that some silver must have dissolved in the cyanide of potassium. According to this the metals may be separated into two divisions with reference to their behaviour towards cyanide of potassium at the ordinary temperature, and without the assistance of a galvanic current; for instance, such as do not and such as do dissolve in cyanide of potassium; to the first division belong platinum, mercury and tin. The second division should again be divided into such as dissolve with decomposition of water, and those in which no such decomposition occurs; to the former belong iron, copper, zinc and nickel; to the latter, gold, silver and cadmium. However, oxygen is necessary in all cases to decompose partially the cyanide of potassium, in order that the metals may combine with the cyanogen.—*Journ. für Prakt. Chem.*, xxxvii. p. 441.

ANALYTICAL CHEMISTRY.

On the Solubility of some Precipitates which occur in Quantitative Analysis. By R. FRESENIUS.

I. Solubility of the Potassio-chloride of Platinum in Alcohol.—*No free Muriatic Acid present.*—*a.* An excess of perfectly-pure recently precipitated potassio-chloride of platinum was digested with alcohol of 0.805 spec. grav. for 6 days, at a temperature of 59° to 68°, in a closed flask, with frequent agitation. 72.5 grm. of the perfectly colourless filtered solution, evaporated in a platinum dish, left 0.0060 grm. residue dried at 212°. Accordingly 1 part potassio-chloride of platinum dissolves in 12083 parts alcohol of 0.805 spec. grav.

b. The same experiment, made with spirit of 0.873, showed that 1 part of the salt required 3775 parts spirit of this strength for solution.

c. With spirit of 0.923, 1 part of the salt dissolved in 1053 parts.

In the Presence of free Muriatic Acid.—Recently precipitated potassio-chloride of platinum was digested in the cold with spirit of

0.873 spec. grav., to which some muriatic acid had been added. 67 grms. of this solution, which was coloured yellowish, left 0.0146 gm. platinum, corresponding to 0.0365 gm. potassio-chloride of platinum; consequently 1 part of the double salt dissolves in 1835 parts of spirit, containing muriatic acid.

II. *Solubility of the Ammonio-chloride of Platinum in Alcohol.*—

No free Muriatic Acid present.—The author found 1 part of this salt to require 26535 parts alcohol of 0.805 for solution, 1406 spirit of 0.873, and 665 parts spirit of 0.223.

In the Presence of Muriatic Acid.—1 part of the double salt dissolved in 672 parts of acidified spirit of 0.873 spec. grav.

III. *Solubility of the Carbonate of Baryta.*—1 part of the recently precipitated salt dissolves in 14137 parts *cold* water, and 1542 parts *boiling* water.

A solution of chemically-pure chloride of barium was treated with an excess of ammonia and carbonate of ammonia, heated gently, and set aside for 12 hours. The filtered solution remained perfectly clear on the addition of sulphuric acid; after standing for a very long time a scarcely perceptible precipitate had separated. 84.82 grms. of the solution, evaporated in a small platinum dish and gently ignited, left 0.0006 residue; consequently 141000 parts of the liquid, containing ammonia and carbonate of ammonia, had dissolved 1 part of the salt.

IV. *Solubility of the Silico-fluoride of Barium.*—1 part of the salt was found to dissolve in 3802 parts *cold* water and 3392 parts water, after being boiled with it, and then allowed to cool. In cold water containing muriatic acid the relation is as 1 part to 733; but on being boiled and then allowed to cool, the relation is as 1 to 640.

V. *Solubility of Sulphate of Strontia.*—In pure water at the ordinary temperature 1 part dissolves in 6895, and in 9638 parts of water at 212°.

In water containing muriatic and sulphuric acid, 1 part requires 11862 parts.

VI. *Solubility of Carbonate of Strontia.*—1 part of the salt requires, according to the author, 18045 parts water for solution; and in water containing ammonia and carbonate of ammonia, 1 part requires 36545 parts for solution.

When a solution of chloride of strontium is precipitated with carbonate of ammonia and ammonia, the filtered solution is not rendered turbid on the addition of alcohol by sulphuric acid.

VII. *Solubility of Carbonate of Lime in Water.*—1 part of this salt dissolves in 8834 parts *boiling* water, and in 10601 parts *cold* water; and in water containing ammonia and carbonate of ammonia 1 part in 65246 parts.

VIII. *Solubility of pure Magnesia in Water**.—Perfectly pure crystallized sulphate of magnesia was dissolved in water, the solution

* The very different results formerly obtained are undoubtedly owing to an imperfectly pure magnesia having been employed in the experiments.

precipitated with carbonate and caustic ammonia, the precipitate most carefully washed (it still contained nevertheless a perceptible trace of sulphuric acid); it was dissolved in pure nitric acid, avoiding an excess of acid, again precipitated with carbonate and pure ammonia, and the precipitate most carefullyedulcorated. The perfectly pure basic carbonate of magnesia thus obtained was ignited in the platinum crucible until its weight remained constant, then digested with distilled water (which left on evaporation not a trace of fixed residue, and was likewise perfectly free from chlorine) for 24 hours in the cold, being frequently agitated. 1 part of pure magnesia was found, on an average of three experiments, to dissolve in 55368 parts cold water. This solution of magnesia has a faint but distinctly alkaline reaction, which may easily be detected by means of slightly reddened litmus paper; it is not rendered turbid by alkaline carbonates either in the cold or on boiling; it likewise remains clear with phosphate of soda, but if ammonia be added it becomes turbid after slight agitation, and soon deposits a distinct precipitate of basic phosphate of ammonia and magnesia.

Pure magnesia, boiled with water, yields a solution which behaves in every respect like that prepared in the cold.

IX. *Solubility of the Carbonate of Lead.*—The author finds that 1 part requires 50551 parts of pure water at the ordinary temperature for solution; this solution is not in the slightest degree coloured by sulphuretted hydrogen.

In water which contained a little acetate of ammonia, and also carbonate and pure ammonia, 1 part of the salt dissolved in 23450 parts; the solution was slightly coloured by sulphuretted hydrogen, and after long standing deposited traces of sulphuret of lead.

Water, containing much nitrate of ammonia besides carbonated and caustic ammonia, dissolves, judging from the colour produced in the filtered solution by sulphuretted hydrogen, somewhat more of this salt than in the preceding experiment.

X. *Solubility of Oxalate of Lead.*—A dilute solution of acetate of lead was precipitated with oxalate of ammonia and ammonia; the liquid filtered from the precipitate after long standing exhibited, on the addition of sulphuretted hydrogen, a faint brownish tint when viewed from above.

XI. *Solubility of Sulphate of Lead.*—1 part of this salt requires 22816 parts of pure water at 52° for solution. In water containing sulphuric acid, 1 part of the salt requires 36504 parts; and in water containing ammoniacal salts and sulphuric acid, no perceptible colour is produced by the addition of sulphuretted hydrogen to the filtered solution.

XII. *Solubility of the Basic Carbonate of Zinc.*—1 part of the salt was found to require 44642 parts water for solution.

XIII. *Solubility of Chloride of Barium in Absolute Alcohol.*—1 part of the salt requires 8108 parts of cold alcohol of 0.795 spec. grav.; and on boiling and then allowing to cool, 1 part dissolved in 6685 parts; but when filtered boiling, 1 part was found to have dissolved in 4857 parts of the boiling alcohol.

XIV. *Solubility of Chloride of Strontium in Alcohol*.—1 part of the salt dissolves in 116·4 parts of cold alcohol of 0·795 spec. grav., and in 262 parts boiling alcohol.—Liebig's *Annalen*, July 1846.

CHEMICAL PREPARATIONS.

Preparation of Uric Acid from Guano. By Dr. A. BENSCH.

THE guano is well boiled for several hours with common potash, slaked lime and a sufficient quantity of water; the solution separated from the residue by a conical bag, evaporated until it forms a thick paste, and thrown whilst hot upon a linen cloth and pressed. The pressed mass is diffused through water, decomposed with common muriatic acid, and the coloured impure uric acid washed with water. The washed uric acid is dissolved in dilute solution of potash, and evaporated until the boiling fluid assumes the consistency of a thick paste, thrown upon a linen bag, and strongly pressed. The pressed urate of potash is boiled with 2 vols. of water, constantly shaken, then rapidly pressed, and this proceeding repeated 3 or 4 times; this causes the mass to swell considerably; hence constant agitation is requisite to prevent its being burnt. If a portion, when dissolved in potash and precipitated by muriatic acid, does not yield a perfectly colourless uric acid, the urate of potash is again completely dissolved in solution of potash, and treated as above.

Lastly, the perfectly white uric acid is dissolved in hot water, to which a little solution of potash is added; the clear hot solution, when poured into muriatic acid, yields colourless uric acid.

The mother-liquors are evaporated and treated as above, the purer solutions of potash being used to dissolve the potash salt in the more impure.

By this method I obtained $2\frac{1}{2}$ lbs. of pure uric acid from 100 lbs. of guano.—*Ann. der Pharm. und Chem.*, lviii. p. 266.

On the Purification of Mercury. By M. ULEX.

In the distillation of mercury we are not only exposed to a very great loss, but the mercury is also not perfectly purified by it. This object is obtained, it is true, by digesting it with acids and perchloride of mercury; but it requires considerable time, as these agents are merely in contact with the surface of the mercury, and can only act upon all its particles by frequently repeated agitation. A solution of perchloride of iron alone possesses the property of dividing mercury to a very great extent. When, for instance, 1 lb. of mercury is treated with 3 drms. *Liquor ferri muratici*, and the same quantity of water, and well shaken for half a minute, the entire mass

is converted, with evolution of heat, into a dark gray mass. The perchloride of iron is reduced to the state of protochloride, while a portion of the mercury is converted into calomel, which latter prevents the globules of mercury running together. If the mercury contain any foreign metals in solution, they are more easily attacked by the chlorine than the mercury, and are either dissolved or precipitated in a pulverulent form. To see whether mercury is contaminated with foreign metals, for instance with tin or lead, merely shaking with air suffices. Chemically pure mercury does not deposit any black powder in this operation, nor does it coat the sides of the glass vessel with a pellicle of mercury. The latter occurs even with $\frac{1}{40000}$ th lead; with $\frac{1}{3000}$ th, the mercury deposits, even after shaking it for 3 minutes, a black powder; with $\frac{1}{1000}$ th lead such a mass of the black powder is obtained, that the surface of the mercury is no longer perceptible. With 4 per cent., and even with 2 per cent. of lead, a solid crystalline compound is obtained. In general the amount of lead does not exceed 1 per cent. In order to effect the purification of the mercury by protochloride of iron, 2 lbs. of mercury are triturated together with 2 oz. of *Liq. ferr. mur.* of 1.48 spec. grav., and as much water, for 10 minutes; then the solution of iron removed by decantation and washing with water, and the mercury deprived of its humidity by gentle heat. On trituration, the greater portion of the mercury runs together; by suitable treatment with muriatic acid, the calomel may be separated from the mercury in the gray powder, and decomposed with protochloride of tin and muriatic acid. If the amount of lead exceed 1 per cent., the operation should be repeated.—*Archiv de Pharm.*, xlv. p. 19.

On the Employment of the Chloride of Soda for detecting the Presence of Guaiacum Resin in that of Jalap. By M. DE SMEDT.

It is a fact, long since known, that chlorine possesses the property of turning the resin of guaiacum blue; according to the author, the chlorides of soda and lime equally possess this property, and may be employed to detect the least traces of guaiacum resin mixed with that of jalap. In fact, 15 centigrammes of jalap resin, mixed with 1 centigramme of guaiacum and dissolved in 4 grms. of alcohol of 0.828, yield with a single drop of the hypochlorite of soda a greenish stripe, which subsides and settles at the bottom of the glass, forming a green stratum perfectly distinct from the supernatant liquid, which retains its primitive colour. This test is so delicate that it is possible to detect $\frac{1}{320}$ th of resin of guaiacum mixed with jalap resin.

F. Boudet states that, on repeating these experiments, he had found them perfectly correct, and also had the opportunity of observing that the chloride of soda detected equally well the presence of guaiacum resin in the resin of scammony as in that of jalap. It is to be hoped that the discovery of so delicate a test will render the adulteration of these resins less common in future.—*Journ. de Pharm.*, Nov. 1846.

PATENT.

Patent granted to Robert Warington, for Improvements in the mode of preserving Animal and Vegetable Substances.

THE first part of this invention consists in preserving animal and vegetable substances by coating them with common glue, gelatine, or concentrated meat gravy, or otherwise, so as to form an air-tight skin or covering over them.

A quantity of glue, gelatine, or concentrated meat gravy, is heated in a suitable vessel, and then the meat, or other substance to be preserved, having been suspended from a string, is dipped into it; and when the coating of glue, gelatine or gravy has solidified, the meat is again dipped; and this is repeated until a hard film or skin, of the desired thickness, has been obtained. Or the substance to be preserved is dipped into a mixture of plaster of Paris and water; and, when the coating has become hard, it is saturated with melted suet, stearine, wax, or other matter that will render it impervious to the air. Or the patentee wraps around the substance to be preserved a thin strap or band of caoutchouc, gutta-percha, or any air-tight membrane, such as water-proof cloth, making each turn lap a little over the other; and when caoutchouc or gutta-percha is used, the edges of the band are cemented together by immersion in boiling water; or the edges of the band may be connected by a cement of caoutchouc or gutta-percha (dissolved in spirits of turpentine, bisulphuret of carbon, or other solvent), or any other suitable cement. Or the patentee covers the surface of the substance to be preserved, either before or after the operation last described, with a varnish or cement of caoutchouc or gutta-percha, or other suitable varnish or cement.

The second part of this invention consists in keeping the articles so coated, or any other animal and vegetable substances, immersed in glycerine, treacle, elaine, oils, and other like matters, not liable to such oxidation, decomposition, or other change from exposure to the atmosphere as would prevent the preservation of the animal and vegetable substances; these matters being kept in tight, but it may be open vessels; and the animal or vegetable substances are only disturbed when removed for use.

Meats for the table should be half-cooked, by boiling or roasting, previous to coating or submersion. When oils are used, the patentee prefers that they should be heated to 220° F.; the articles are then immersed, and the oil is allowed to cool. Fats, oils and waxy substances, which present a solid appearance at the ordinary temperatures of the atmosphere, should of course be melted previous to the immersion of the articles therein.—Sealed March 5, 1846.

THE CHEMICAL GAZETTE.

No. C.—December 15, 1846.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the peculiar Phenomenon observed in the Solidification of Silver.
By H. ROSE.

ACCORDING to Level the frothing of silver is produced by the protoxide of copper which is absorbed into the cupel, being converted into peroxide by the oxygen given off by the silver on solidification. An important addition to our knowledge of this phenomenon is the fact that it may likewise occur when the access of air is prevented. If a regulus of pure silver be fused under a layer of potash or common salt, the regulus is found after cooling with a bright surface beneath the saline crust; but if a few crystals of saltpetre or cubic nitre be thrown upon the fused mass, and the whole allowed to cool slowly, it will be found that the regulus of silver beneath the fused salt has frothed just as much as if the silver had been fused with access of air. The layer of salt was generally from 3 to 4 inches high; and as the specific gravity of the salt is more than double that of water, the pressure under which the frothing took place was therefore not quite so great as that of a foot of water. It is remarkable that the nitre in this experiment yields its oxygen to the silver, as it is specifically lighter than the salts employed, and consequently must float upon them. In order that the frothing may take place under a saline coating, this must consist of readily fusible salts, so that the silver can solidify before them. If, after the addition of the nitre, the firing is much increased, the regulus is frequently found after cooling to possess a smooth surface; but this undoubtedly only occurs when the frothing has already taken place, and the regulus again fused. When chloride of silver is reduced by fusion with an alkaline carbonate, no frothing occurs, although oxygen and carbonic acid escape. The reason is that the reduction of the chloride of silver takes place at a tolerably low temperature, so that when the silver begins to fuse the gases have already escaped. No frothing therefore occurs when a substance which parts readily with its oxygen is thrown upon the fused mass, for instance, chlorate of potash; while chromate of potash, which does not readily part with its oxygen, causes the silver to froth. When silver is melted under a pasty saline crust, for instance beneath common salt and powdered

Chem. Gaz. 1846.

manganese, no frothing generally occurs, even when sufficient oxygen is conveyed to the silver.

On fusing silver beneath a layer of common salt, there is always a loss of silver. Winckler had already shown that metallic silver at a bright red heat decomposes the salt, forms chloride of silver, and the more of it the finer the silver is divided. Plattner confirmed that statement, and found that the quantity of chloride of silver is not increased by additions of peroxide of iron and peroxide of copper. The author likewise obtained the same results as Winckler; the longer the fusion was continued, the more chloride of silver was formed. A regulus, weighing 27 grms., fused with 2 oz. of chloride of sodium for $2\frac{1}{2}$ hours, at a very high temperature, had decreased 0.75 gm., but at the same time the whole of the chloride of sodium had been volatilized. When the fusion was continued less time, the loss in silver was less. No alkaline reaction could be observed in the solution of the fused mass, nor did the fused silver, when placed in contact with water, disengage any bubbles of gas; so that the eliminated sodium appears to have been volatilized as soda along with the chloride of sodium. This is also rendered more probable from the formation of chloride of silver being increased by fusing silver and common salt, and facilitating the oxidation of the sodium in the fusing mass by the addition of manganese. But in this case there is likewise no alkaline reaction, nor any formation of manganate of soda; the simultaneous presence of soda and chloride of silver is also barely possible, as they would immediately decompose each other on being heated. It is also on that account that no chloride of silver is formed when nitrate of soda is added to the chloride of sodium; but a slight loss is experienced by the frothing of the silver. This however also happens when silver is melted with common salt and carbonate of soda.

Copper is likewise able to decompose the chloride of sodium in the same way as silver. When copper is fused under a layer of common salt, the vapours of the salt escape with an azure-blue flame. In the solution of the fused residue, which does not possess an alkaline reaction, copper may be detected by ammonia. When an alloy of copper and silver is melted, protochloride of copper, and not chloride of silver, is formed, even when the silver preponderates in the compound. When ordinary clay crucibles are used for the experiments, the volatilization of the chloride of sodium is far more considerable than in Hessian crucibles, evidently owing to the greater porosity.—Poggendorff's *Annalen*, lxviii. p. 283.

On Crystallized Bile. By FR. VERDEIL.

This compound was obtained by evaporating the bile of a fresh ox-gall bladder to dryness in a water-bath, and treating the residue with about 20 parts of absolute alcohol; the mucus was thus left in an insoluble state, whilst the bilate of soda was readily dissolved by the absolute alcohol. The alcoholic solution was filtered from the mucus and treated with animal charcoal for some time, whereby the

originally green solution became perfectly white. Æther was then cautiously added to this purified alcoholic solution until it began to become turbid and milky; the vessel was then carefully closed and set aside. The crystallization began in a short time. The bilate of soda subsided on the sides of the vessel in fine needles, which united into concentric groups. At the end of 24 hours, after which time but little subsided, the mother-liquor was poured off the crystals; the latter were collected on a filter, carefully washed with æther free from alcohol, and dried over sulphuric acid. To obtain the crystals, it is of great importance that the solution of the bilate of soda in absolute alcohol should have the above degree of concentration. If the solution be more concentrated, it becomes turbid considerably sooner on the addition of æther, but without the formation of crystals; if more æther be added, the bile is precipitated in an amorphous state as a smeary mass.

The crystals thus obtained are not pure, but contaminated with a considerable amount of chloride of sodium. On treating the dried bile with absolute alcohol, a considerable quantity of chloride of sodium is always dissolved, which is completely precipitated on the subsequent addition of æther, and subsides in small crystals with the crystals of bile. The removal of this impurity is difficult. Chloride of sodium is somewhat soluble in alcohol containing bile at ordinary temperatures; no trace however is taken up at a lower temperature artificially produced. This peculiarity enabled me to obtain it sufficiently free from chloride of sodium. The alcoholic solution which I thus procured was at once evaporated to dryness in a water-bath, and used for analysis. The substance is readily powdered after having been dried at 212° , and resembles in every respect bile freed from fat and mucus in the ordinary way. It yielded the following results:—

	I.	II.	III.	Mean.	Equiv.	Calculated.
Carbon. . . .	59.84	59.77	60.07	59.87	44 =	60.35
Hydrogen . . .	8.73	8.80	9.20	8.91	40	9.15
Nitrogen ..	4.11	4.33	..	4.22	1	3.24
Sulphur ..	3.78	3.89	..	3.83	1	3.66
Oxygen ..	16.45	16.32	..	16.18	9	16.46
Soda.....	7.09	6.89	..	6.99	1	7.15
	100.00	100.00				

Per-cent. composition
of the pure acid.

Carbon	64.33
Hydrogen	9.59
Nitrogen	4.53
Sulphur	4.11
Oxygen	17.44

The atomic weight of the acid is 5193, the atomic weight of soda being 391.

The bilate of soda yields a compound with basic acetate of lead, which I examined. It has a resinous aspect, and when dried at 212°

is readily powdered. The compound becomes very soft in hot water, again assuming its hardness in cold; it dissolves in alcohol. It yielded—

Carbon.	40.68
Hydrogen	4.97
Oxide of lead	35.26

Although Demarçay formerly proved that bile yields a resinous substance and taurine when boiled with muriatic acid for some time, still it was doubtful whether these products of decomposition did not exist ready formed in the gall-bladder. To remove this doubt, I treated the pure crystallized bile with muriatic acid, and my results perfectly confirm those of Demarçay. I added muriatic acid to a concentrated solution of the crystals; the fluid was thus rendered at first white; oily drops speedily separated upon the surface, which continued to increase in consistence, and on long boiling finally changed into a resinous substance (choloidic acid), which swam in the liquid. After boiling for some hours, I filtered off the choloidic acid which had formed, and evaporated the filtrate. The residue was again dissolved in alcohol, and then partly evaporated, whereupon most of the chloride of sodium crystallized out. On still more evaporating the liquid, it yielded crystals of taurine on cooling, and on the further addition of alcohol.—*Ann. der Pharm.*, September.

• *On Glycyrrhizine.* By Dr. T. LADE.

This investigation was undertaken with a view to obtain more accurate information with respect to the condition of the glycyrrhizine in the root and in the extracts so frequently used in medicine. To prepare it, the finely-cut liquorice root was exhausted with cold water, and the highly coloured extract concentrated after filtration; the green nitrogenous body which separated by the action of the heat again removed by filtration, and a dilute acid added to the clear liquid as long as an abundant precipitate was produced. The light-coloured deposit, which was at first flocculent, soon caked together to a tenacious pitch-like blackish-brown mass, which was separated by decanting the supernatant liquid. After frequent kneading in acidified, and then in pure cold water, the substance was obtained free from acid and inorganic constituents. It became brittle and shining by drying in the water-bath; it was now pulverized, dissolved several times in absolute alcohol, and again evaporated at a very gentle heat. When sulphuric acid is employed to precipitate it, care should be taken to remove every trace of acid before drying in the water-bath, as it decomposes the glycyrrhizine at an elevated temperature, and produces considerable loss.

Glycyrrhizine, as obtained on evaporation of the alcoholic solution, is a shining, transparent, brown mass, which yields a brownish-yellow powder. It is but little soluble in cold water, especially when this contains a little free acid; it is more readily soluble in boiling water, with the diffusion of a peculiar odour, which at first calls to

mind that of spirit containing fusel oil, and after long standing nearly resembles that of a decoction of liquorice. The hot saturated aqueous solution solidifies on cooling to a brown transparent jelly; if an excess of glycyrrhizine be conveyed into the hot solution, it cakes together to the above-described brown pitchy mass; its taste is very sweet, but accompanied with a peculiar disagreeable bitter. It dissolves very readily in alcohol, especially when absolute, but is not dissolved in the least by either cold or boiling æther. The yellow colour appears peculiar to the glycyrrhizine, as it was impossible to separate it. Chemically pure animal charcoal has no action upon solutions of glycyrrhizine, either in the cold or when heated; but if it contain inorganic salts, these enter into combination with the organic body, and the filtered solution has lost its colour and sweet taste. The aqueous, as well as the alcoholic solution, has a strong acid reaction upon blue litmus-paper. Alkalies colour the solution deep yellow-brown, and but a minute quantity is requisite to render a comparatively large amount of glycyrrhizine soluble in cold water.

The solutions of glycyrrhizine obtained with the assistance of an alkali yield light flocculent precipitates with most acids, which are partially soluble in an excess of the precipitant, for instance when acetic acid is used. The whole of the acid may be removed by long-continued kneading.

Numerous experiments were made to prepare picronic acid from pure glycyrrhizine, but without success; it only yields with concentrated, or by boiling with dilute nitric acid, a bitter substance, which will be hereafter described. In hydrated sulphuric acid it dissolves with a brown colour, and is again precipitated on the addition of water.

It is not converted into grape-sugar by continued digestion with dilute sulphuric acid, nor can it be fermented by means of yeast; it must consequently be excluded from the class of saccharine substances.

Glycyrrhizine exists in the root and its extracts in combination with inorganic bases as lime and ammonia, and is therefore separated by the addition of a stronger acid. The reason that a further quantity of acid precipitates still more glycyrrhizine from an already acid extract, is owing to its being far less soluble in water, containing much free acid; the large quantity of ammonia contained in the infusion is rendered evident even in the cold by the addition of milk of lime, and still more so on the application of heat. Dried at 212° , and burnt sometimes with chromate of lead, sometimes with oxide of copper, it yielded the following results:—

	Equivs.					
Carbon	61.26	61.10	61.09	60.61	36* =	61.3
Hydrogen	7.31	7.39	7.21	7.09	24	6.8
Oxygen	31.52	31.51	31.70	32.03	14	31.8

It was found impossible to obtain the glycyrrhizine perfectly free from nitrogen, for instance by combining it with bases, and then

* M. Vogel, Jun., in his analysis of pure glycyrrhizine and its combination with lead, arrived at the formula $C^{16}H^{12}O^6$. See Chem. Gaz., vol. i. p. 284.

separating it again by an acid; it never however amounted to more than 0·03–0·06 per cent., and must therefore be regarded as an impurity. I convinced myself of the absence of sulphur by boiling it with caustic potash and adding acetate of lead.

Glycyrrhizine enters into combination with bases; thus with acetate of lead it forms a yellow flocculent precipitate, which becomes granular at a temperature at which the surrounding liquid freezes, and can easily be washed; with a solution of silver it yields a white precipitate, which from its solubility could not be obtained sufficiently pure for analysis; it also forms combinations with baryta and lime.

Lead Compound.—A solution of glycyrrhizine in spirit was precipitated in the cold with acetate of lead, and the precipitate edulcorated on a filter. I obtained two different combinations according to the nature of the liquid used for washing it; that edulcorated with water contained the least lead, that with spirit the most; both dried at 212° and pulverized, gave yellow powders, scarcely differing from one another in colour; treated with spirit and sulphuric acid, they were decomposed (most easily by the application of a gentle heat) into sulphate of lead and an alcoholic solution of glycyrrhizine, a property which very much facilitated the determination of the atomic weight of these compounds.

The analysis of the precipitate washed with spirit gave the following results:—

Carbon	37·46	36 =	38·77
Hydrogen	4·37	22	3·95
Oxygen	18·37	12	17·24
Oxide of lead	39·80	2	40·04

The following composition was found for the precipitate washed with water:—

Carbon	45·98	36 =	47·52
Hydrogen	5·49	23	5·05
Oxygen	23·89	13	22·88
Oxide of lead	24·64	1	24·54

leading to the formula $C^{36} H^{22} O^{12} + \begin{Bmatrix} PO \\ HO \end{Bmatrix}$

From these it is evident that the rational formula for glycyrrhizine is $C^{36} H^{22} O^{12} + 2HO$, which $2HO$ can be entirely or in part replaced.

Lime Compound.—When, in the preparation of glycyrrhizine, the extract is supersaturated with finely-divided lime-paste, and boiled until all ammoniacal odour has disappeared, a dirty orange-coloured residue is obtained on filtration, which is very sparingly soluble in water, and imparts to it a sweet taste; the residue on the filter, which is mixed with an excess of lime, is suspended in water supersaturated with washed carbonic acid, heated to expel the excess of carbonic acid, filtered and evaporated to dryness. The solution of this salt resists the action of free carbonic acid, as evident from its mode of preparation. It is wholly insoluble in spirit; from the aqueous solution, which has an extremely sweet taste, the gly-

cyrrhizine is separated by acids with all its properties. It was not found possible to obtain this salt perfectly pure; the amount of lime varied in different preparations; but the per-centage composition of the glycyrrhizine in the salt agreed with that found for pure glycyrrhizine.

Product of Oxidation.—By dissolving pure glycyrrhizine in ordinary or concentrated nitric acid, and subsequently adding water, a yellowish-white caseous precipitate is formed, which, washed with water on the filter and dried in the water-bath, forms a yellowish-white loose powder. The same results are obtained when the extract of the root is concentrated and boiled with nitric acid until the violent frothing ceases; when the quantity of the still undecomposed nitric acid is too small to hold the new body completely in solution, it separates partially as a brownish-yellow resinous mass, which is tenacious whilst warm and brittle in the cold; the portion dissolved in the dark-coloured liquid is separated for the greater part by water as a yellow precipitate. The product obtained in either of these ways is purified by washing with water, dissolving it in concentrated nitric acid, boiling the solution for some time in a flask, and when cold pouring it into agitated distilled water. The precipitate thus obtained forms, after washing and drying, a yellow, light powder.

It dissolves in alcohol and in æther, from which it is for the greater part separated by water; it is very sparingly soluble in water, but imparts to it an extremely bitter taste and acid reaction; it is not in the least altered by boiling for several days with the strongest nitric acid, which proves the absence of picronic acid and xyloidine. Heated on platinum foil, it puffs up, and burns like wax. It is very readily soluble in water containing an alkali, its bright yellow passing into a deep orange colour; acids precipitate it unaltered. It is thrown down from the pure, and also from the alkaline solution, by several metallic salts in combination with the corresponding oxides; but these precipitates are, as in the case of glycyrrhizine, mostly so soluble in the liquids employed for washing them that it is impossible to obtain them pure. This body gave on analysis—

Carbon	57.40	57.31	56.98	36 =	57.6
Hydrogen	6.00	6.09	6.00	23	6.1
Oxygen	36.60	36.09	36.42	17	36.3

and an amount of nitrogen which varied in different preparations between 0.1 and 0.6 per cent., and cannot therefore be regarded as entering into the composition of the substance.

The formation of this product from glycyrrhizine, $= C^{36}H^{24}O^{14}$, may be explained by the substitution of 1O for 1H and the addition of 2O. A combination of this body with lead may be obtained by precipitating a spirituous solution with neutral acetate of lead, and washing the precipitate with dilute spirit: when dried it formed a beautiful lemon-yellow powder, but the results obtained on its analysis varied with respect to the amount of lead, and it consequently requires further examination.—Liebig's *Annalen*, August 1846.

' *On the Formation of Lactic Acid.* By H. WACKENRODER.

The author had previously announced that he had succeeded in converting sugar of milk into lactic acid by means of vegetable albumen; he returns to the subject in the present notice, in which he also describes the use of animal albumen for the same purpose. The conversion of milk sugar by other proteine compounds than caseine is interesting in many respects; but this question would acquire far more importance were it to change into certainty the presumption that every kind of sugar is susceptible of being converted in the same manner into lactic acid, and that this acid is generated whenever the alcoholic fermentation of the sugar or the conversion of the gum, principally of the dextrine, has failed. The author thinks that the free acid of beer, which is generally considered to be malic acid, is lactic acid; and according to the researches in which he is at present engaged, this acid not only occurs in the beers which have done fermenting, but the fresh wash, and even the malt itself, contains a certain quantity.

To ascertain the action of vegetable albumen on milk sugar, the juice of several plants separated from the chlorophylle was placed in contact for several weeks with milk sugar, and some powdered carbonate of lime, at a temperature of about 68° F., stirring it frequently. In all these experiments lactate of lime was obtained, which was very easily purified.

The resemblance of animal albumen to vegetable albumen induced the author to employ also the former, in order to effect the metamorphosis of the milk sugar; he first took the white of a fresh egg, dissolved it in distilled water, and followed the process described above, but the sugar underwent no alteration. He then placed the coagulated white of egg for some weeks in contact with water, and when it had become acid he added to it some milk sugar and carbonate of lime. After standing for six weeks in a warm chamber, the greater portion of the milk sugar had changed into lactic acid, and very beautiful groups of crystals of lactate of lime were obtained from it. M. Wackenroder concludes from these experiments that the albumen of the white of egg is not able to convert the milk sugar into lactic acid until after its coagulation and passage into acid fermentation; and that the negative result, obtained with the fresh white of egg, should probably be attributed to its alkalinity.—*Archiv der Pharm.*, June 1846, p. 257.

On the Composition of Sugar of Gelatine. By H. LAURENT.

The author has examined some sugar of gelatine in very beautiful crystals, and found 32.10 per cent. C, 6.66 H, 18.92 N, whence he deduces the formula $C^4 H^5 NO^4$; this gives C = 32.0, H = 6.66, N = 18.66, O = 42.68. According to this, sugar of gelatine would be isomeric with urethylane. When 1 equiv. water is added to hippuric acid, we obtain $C^{18} H^9 NO^6 + HO = C^{14} H^6 O^4 + C^4 H^5 NO^4$.—*Comptes Rendus*, xxii. p. 789.

Experiments on the Absorption of Arsenic by Plants.

By Dr. HERBERGER.

The experiments were made in the summer of 1843 in a loamy and in a sandy soil containing very little humus, with seeds of *Triticum spelta* which had been steeped in white arsenic. Although all the parts were examined both before the formation of stem, before flowering, and also just before ripening, not a trace of arsenic could be detected. In each experiment at least 250 grms. of the substance were carbonized with sulphuric acid, and then immediately tested according to Marsh's process, as well as by the method of Reinsch.—*Jahrb. für Prakt. Pharm.*, xii. p. 286.

• *Oxalate of Lime in Cereus senilis.*

According to Lucas, the stem of this plant is filled to such an extent with crystals of oxalate of lime, that the vegetable substance almost entirely disappears in comparison. 100 parts of the stem contained 80 parts oxalate of lime.—*Buch. Rep.*, xliii. p. 106.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Adulteration of White Lead. By M. LOUYET.

It is really deplorable to see to what an extent certain chemical products are sophisticated; there is no knowing how far these villainous frauds, which injure our health no less than our purse, will go, for the pharmaceutical are sophisticated as much as the chemical products employed in the arts.

I lately received three samples of white lead, of different qualities, destined for exportation. It is probable that the distant destination of these products induced the manufacturer to believe that it was useless to keep within any bounds, and that the ignorance of the consumers would prevent them from knowing that what was given them for white lead might quite as well be called sulphate of baryta as carbonate of lead.

1 grm. of sample No. 1, heated to redness in a platinum crucible until completely converted into litharge,	} 0.100
lost	

A second calcination produced no further loss.

1 grm. of sample No 2 lost by similar treatment	0.049
---	-------

1 grm. of No. 3 lost	0.037
----------------------------	-------

The product of the calcination of No. 1 was boiled with pure nitric acid, the liquid diluted with water, and again boiled. There remained a yellowish residue, although the liquid was strongly acid; it was collected on a filter, and well washed with boiling water, dried and calcined; it weighed 0.305. I must not omit to observe that

the residue yielded by the calcination of the white lead No. 1 was of a darker red than that yielded by No. 2, and this more so than the residue of No. 3, which was nearly white. The residue left by No. 1, after treatment with nitric acid, gave, on being heated with soda upon charcoal before the blowpipe, a fused residue, which, placed upon a bright piece of silver and then moistened, produced a permanent black stain. This character belongs to the sulphates. It was proved that the sulphate mixed with the carbonate of lead was sulphate of baryta. The solution obtained by digesting the white lead No. 1 with nitric acid was precipitated by sulphuric acid; the sulphate of lead, after having been heated to redness, weighed 0.765. This quantity of sulphate of lead contains 0.563 protoxide, which requires 0.111 carbonic acid to form the neutral carbonate, producing 0.674 carbonate. According to calculation from the oxide of lead found, I should have 0.111 carbonic acid; and by calcination, which converts the carbonate into oxide, I found only a loss of 0.100. This difference arises, it is true, from the whole of the oxide of lead not being in the state of carbonate; a small portion is in the state of hydrate; but as the equivalent of water is far less than that of carbonic acid, it follows that, by calculating the whole of the oxide as combined with carbonic acid, I obtained too high a figure; it is requisite therefore to subtract 0.011 from 0.674, which leaves 0.663.

The white lead No. 2 was treated in the same manner; the portion not dissolved by nitric acid, washed, dried and ignited, weighed 0.660. The sulphate of lead yielded by the nitric solution = 0.360, containing 0.264 protoxide of lead, which combined with 0.052 carbonic acid to form 0.316 carbonate. In this case the number calculated for the carbonic acid differs very little from that found. But in this instance, as in the preceding, the amount of carbonate of lead obtained is too low, and the loss must be referred to it. 1 grm. of No. 3 left a residue, on treatment with nitric acid, which weighed 0.718; it afforded 0.277 sulphate of lead, containing 0.203 protoxide, which combines with 0.040 carbonic acid, forming 0.243 carbonate of lead.

According to these analyses the white leads have the following composition:—

1 grm. of No. 1 contains 0.695 white lead and 0.305 sulphate of baryta.

...	No. 2	...	0.340	...	0.660	...
...	No. 3	...	0.282	...	0.718	...

It is not without reason therefore that I stated that these articles might as well be sold under the name of sulphate of baryta as under that of sulphate of lead.—*Bulletin de Musée du l'Industrie*, 1846.

Method of cleansing Retorts and Glass Vessels. By H. REINSCH.

In cleansing glass vessels with sand there is the danger of scratching them with the particles of quartz, which causes the vessels to

fly. Shot being, for well-known reasons, wholly objectionable for this purpose, the author recommends pieces of coal about the size of a pea, which are equally efficacious, and do no injury to the glass.—*Jahrb. für Prakt. Pharm.*, xii. p. 367.

How to prevent Iron from Rusting.

Zeni recommends, for this purpose, 80 parts of pounded and very finely sifted brick-dust, which is to be mixed with 20 parts of litharge. The mixture is ground upon a slab with linseed oil to a thick paste, and diluted with oil of turpentine. Before use, the iron, even when it is new, should be rubbed quite clean. M. Zeni asserts that iron, which had been twice painted with this and exposed for some time daily to the action of the sea, had remained entirely free from rust.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Nov. 2, 1846. (The President, Professor Graham, in the Chair.)

“On the Supply of Iodine from the Kelp of Guernsey,” by the President.

The sea-weed from the rocky shores is largely collected by the inhabitants of the island, as is well known, laid out to dry in the fields, and afterwards burned as fuel in their houses, the ashes being kept and used as manure. These ashes are likely to contain more iodine than ordinary kelp, from being the product chiefly of the deep-sea fuci, and from the low temperature employed in the combustion of the dried plants. This was found to be the case on testing the Guernsey kelp for iodine; and the attention of manufacturers was accordingly called to it, as a source of that article which might probably be had recourse to with profit, with the present high price of that drug.

“Analysis of a Peruvian Alloy,” by Mr. H. How.

This alloy was taken from a human skull found in Peru, and supposed to be that of an ancient Peruvian chief or inca. It consisted of gold, 38.93; silver, 54.82; copper, 5.80. It is questionable whether this is an artificial alloy, or the crude product of a rough metallurgic process.

“On the Gun-cotton,” by Mr. E. F. Tschemacher.

Nov. 16, 1846. (The President, Professor Graham, in the Chair.)

“On the Gaseous Products from Gun-cotton decomposed by Heat,” by Robert Porrett, Esq. and E. F. Tschemacher, Esq.

“On the Presence of Phosphoric Acid in the Felspar of Jersey,” by George Fownes, Ph.D.

After alluding to a previous communication on the presence of phosphoric acid in certain rocks and minerals of volcanic origin, and the results of which have been called in question by Professor Kersten, Mr. Fownes proceeds to show that by a treatment similar

to that before adopted he could readily detect the phosphoric acid in the partially decomposed felspar of Boullay Bay, Jersey.

"Analysis of the Water from the King's Well, Bath," by Messrs. Muck and Galloway.

The whole method of analysis pursued in this investigation is first given in detail, and the authors sum up with the following results in the imperial gallon:—Carbonate of lime, 8·820; carbonate of magnesia, 0·329; carbonate of iron, 1·064; sulphate of lime, 80·052; sulphate of potash, 4·641; sulphate of soda, 19·229; chloride of sodium, 12·642; chloride of magnesium, 14·581; silica, 2·982; with traces of iodine and oxide of manganese = 144·340. Its specific gravity is 1·0025, and its temperature 115°, the atmosphere being 68° at the time.

"Analysis of Sand from St. Michael's Bay, Normandy," by Mr. Gladstone.

This sand is carted away at low tide to great distances, and is employed as a manure. It consists of carbonate of lime, 44·9; salts of sea water, 0·8; organic matter, 5·2; iron, siliceous grains, and debris of granite, 49·1.

Dec. 7, 1846. (The President, Professor Graham, in the Chair.)

"On the Chemical Composition of Gun-cotton," by Messrs. Porrett and Teschemacher.

A communication from Mr. Teschemacher was read before this Society on the 2nd of November last, giving the composition of this new explosive substance, as deduced from synthetical experiments, as follows:—

39·25 of cotton deprived of its constitutional water.
60·75 of nitric acid.

100·00

In the present paper Messrs. Porrett and Teschemacher showed that this composition agreed very closely with the formula



and the analytical results, the principal subject of this paper, also confirmed it. It may be expressed in centesimal proportion as—

Carbon.	20·00	Or {	Lignine dried at 350° . .	40 parts.
Oxygen { 17·78 }	62·22		Nitric acid	60 ...
{ 44·44 }				
Hydrogen	2·22			100 parts.
Nitrogen	15·56			
	100·00 parts.			

As this very nearly agrees with Mr. Teschemacher's synthetical results, it was taken as the composition of nitrated lignine in these experiments, and considered as identical with gun-cotton.

Messrs. Porrett and Teschemacher then pointed out the improbability of Mr. Crum's mechanical view of the combination of nitric acid with cotton, and dwelt upon the necessity of considering it as a strictly chemical compound.

They then reverted to their joint communication "On the Gaseous Products of Gun-cotton decomposed by Heat," read before the Society on the 16th November last, stating that they had some important additions to make in that paper with regard to the quantity of hydrogen and nitric oxide formed by combustion, and also as to the quantity of mixed gases obtained from a given weight of cotton. They now stated the true quantities of mixed gases to measure 100 volumes from 52.53 grs. of gun-cotton, and gave the following composition:—

	Relative volumes.	Cubic inches.	grs.
Carbonic acid	2	14.286	6.759
Nitrogen	1	7.143	3.965
Nitric oxide	5	35.715	11.478
Carbonic oxide	5	35.715	10.714
Hydrogen	1	7.143	2.154
		100.002	35.070

It follows that if 52.53 grs. of gun-cotton give the above results, 100 grs. would give 64.550 grs. of the mixed gases, and that they would give as the ultimate elements

15.030 grs. carbon.
31.680 ... oxygen.
17.840 ... nitrogen.
64.550 grs.

Water separated by passing the gases from the combustion-tube through a tube containing chloride of calcium, to be added to the gaseous products

20.000 ...

A crystalline deposit, both in the combustion-tube and in the one leading from it, together with 5 grs. of carbon lining the combustion-tubes; weight together 13.125 grs., of which 8.125 was anhydrous oxalic acid

5.000 ... carbon.
8.125 ... oxalic acid.

The total product 97.675

If these products are collected, it is found that they consist of—

Carbon.	{ in the gases	15.030	} 22.738
	{ in the anhydrous oxalic acid	2.708	
	{ in the residue	5.000	
Oxygen	{ in the gases	31.680	} 54.876
	{ in the water	17.780	
	{ in the oxalic acid	5.416	
Hydrogen in the water		2.220	
Nitrogen in the gases		17.840	
		97.674	
Leaving a deficiency, from unavoidable errors } in the experiment, of		2.326	
		100.000	

If these ultimate elements be compared with the composition assigned in the commencement of this paper to nitrated lignine or gun-cotton, the following near approximation will be observed :—

	From the analysis.	From the composition of nitrated lignine.
Carbon	22.738	20.000
Oxygen	54.876	62.220
Hydrogen	2.220	2.220
Nitrogen.....	17.840	15.560
	97.674	100.000

The differences no doubt arise from the difficulties of the experiments necessarily performed on very small quantities, and multiplied, when brought out by calculation, as 100 grs.

Messrs. Porrett and Teschemacher then endeavoured to make a complete combustion of all the elements of the gun-cotton, by combining it with chlorate of potash, but could not get a sufficient quantity of chlorate to adhere to it for that purpose; but a combustion effected with 1 gr. of the cotton with 0.4 gr. of chlorate of potash, gave the following result:—

Carbonic acid	0.420 gr.	} containing 0.200 carbon.
Carbonic oxide	0.198 ...	
Nitrogen.....	0.178 ...	
Water.....	0.200 ...	
	0.996 gr.	

which differs but little from the result obtained from the imperfect combustion.

M. Pelouze communicated to the Academy of Sciences at Paris, on the 23rd November, a note from Messrs. Fordos and Gelis, stating that they had obtained from gun-cotton a "cyanic compound;" this tends to confirm the discovery of Messrs. Porrett and Teschemacher, of the presence of cyanogen among the gaseous products which they had previously announced in their paper before alluded to, and read before the Chemical Society on the 16th November last.

A view may be taken of the composition of gun-cotton agreeing with the ultimate result, but arranging the elements differently, by subtracting 1 atom of oxygen from the nitric acid, and adding it to the lignine; gun-cotton would then be formed of nitrous acid + oxide of lignine; this hitherto unknown oxide may possess alkaline properties, and thus account for the singular fact of the non-acidity of gun-cotton.

Messrs. Porrett and Teschemacher concluded by stating that it was their intention to try to establish this composition by experiments; and that, in fact, they had tried the action of a small galvanic battery in decomposing gun-cotton, but without any decided results; on the first vigorous action of the battery, reddened litmus-paper was made blue in the negative cell, but as the power of the battery subsided this effect disappeared.

INDEX TO VOL. IV.

ACETIC acid, preparation of, 322.

Acids and alkalies, on the constitution of aqueous solutions of, 227.

Agaricus graveolens, analysis of the ashes of, 385.

Albumen, estimation of, 283; amount of sulphur in, 363.

Albuminose, amount of sulphur in, 363.

Aldehyde, preparation of, 322.

Ale, improvements in the manufacture of, 288.

Ales, Burton and pale, examination of, 78.

Allitric acid, formation and composition of, 110.

Alloxan, on the preparation of, 1, 23, 109.

Alloxanic acid and its salts, 2; on the products of the decomposition of, 96.

Alloxantine, products of the decomposition of, 110.

Alloy, analysis of a Peruvian, 495.

Allyle, on the sulphuret and sulphocyanuret of, 252.

Alum, improvements in the manufacture of, 168.

Alumina, on the detection of, 127; solubility of, in solution of ammonia, 347; on native sulphate of, 422.

Ammonia, on the amount of, in the atmosphere, 34; analysis of compounds of, 144; on an impurity occurring in, 283.

— and magnesia, on the bibasic arseniate of, 296.

— and prussian blue, on a combination of, 157.

Amyle, on the cyanurate of the oxide of, 420.

Angelica officinalis, on the volatile acids in, 129.

Angelie acid and salts, 130; on the preparation and properties of, 223.

Aniline, researches on, 22; on some compounds of, 213, 214; compounds of phosphoric acid with, 286.

Animal and vegetable substances, mode of preserving, 484.

Anthon, E. F., on the solubility of gypsum in water and in a solution of chloride of sodium, 173; on the formation and preparation of hyposulphite of

soda, 325; on the formation of the sulphite of nitric oxide, 335.

Antimony, on the salts of, 444; new double salts of, 76; separation of, from tin, 105; preparation of the golden sulphuret of, 462.

Arppe, A. E., on the oil of *Monarda*, 474.

Arsenic, atomic weight of, 64; presence of, in soot, 114; magnesia an antidote for, 316; estimation of, in alloys, &c., 159; separation of, from gold, platinum and tin, 39; new process for detecting, in organic mixtures, 137; method of distinguishing minute traces of, from antimony, 106; absorption of, by plants, 493.

Arsenic acid, separation of, from arsenious acid, 296.

Arsenious acid, magnesia an antidote for, 293.

Ashes of plants, analyses of the, 229.

Assafoetida, on the composition of, 444.

Austin, R., on a new test for prussic acid, 220.

Aventurine, on the production of artificial, 141; analysis of, 203.

Badianic acid, 421.

Bankart, F., on treating certain metallic ores, 128.

Barium, atomic weight of, 64.

Barnes, Mr., on the manufacture of certain agents used in dyeing, 127.

Barral, M., on some new substances from tobacco, 76; on the precipitation of gold in the metallic state, 326.

Barreswil, M., on a new method of separating cobalt from manganese, 159.

Baryta, method of distinguishing, from strontia by the blowpipe, 299; caustic, preparation of, 461.

Bdellium, method of distinguishing, from myrrh, 225.

Bees-wax, examination of, 12; products from the dry distillation of, 12; from the action of nitric acid on, 13.

Benckiser, J. A., on the employment of Rochelle salt in dyeing, 125.

Bensch, Dr. A., on the purification of hippuric acid, 461; on the preparation of uric acid from guano, 482.

- Benzoic acid, researches on, 14; preparation of, 202.
- Berlin, M., on the atomic weight of chromium, 154.
- Berthet, M., on a method of ascertaining the purity of iodide of potassium, 457.
- Bertozi, M., on the occurrence of copper in biliary calculi, 53.
- Besanez, Dr. G., on the production of taurine from human bile, 280.
- Bile, on the presence of copper in the, 291, 383; conversion of sugar into fat by, 242; on the body produced by the joint action of sulphuric acid and sugar on, 278; determination of the sulphur in, 471; on crystallized, 486.
- , human, on the production of taurine from, 280; on the constitution of, 294.
- Bleibtreu, Dr., researches on coumarine, 267.
- Bley, Dr., on the preparation of benzoic acid, 202; observations on myrrh and on a method of distinguishing it from bdellium, 225.
- Blood, researches on the, 289; on the extractive matters of the, 73; on the presence of carbonates in the, 94, 209; on the colour of the, 417; detection of pus in, 427.
- Blue, improvements in the manufacture of, 128.
- Böttger, Prof., on a new and simple method of preparing chloric acid, 121; on the reduction of chromic acid by ammonia, vapour of alcohol, &c., 152; on gold, silver and copper bronzes, 366; on the amalgamation of iron and steel, so as to prepare them for fire-gilding, 405; on the manufacture of lucifer-matches without sulphur, *ib.*; on a method of colouring German silver blue, 464.
- Bolley, Dr. P. A., on the preparation of chromic acid, and on a peculiar behaviour of this acid towards sulphuric acid, 139.
- Bones of pigs, on the development of mineral substances in the, 392.
- Boracic acid, separation of, from phosphoric and fluoric acids, 186.
- Boracic æther, preparation and composition of, 287.
- Bottles, &c., improved method of stoppering, 248.
- Bouchardat, M., on the employment of essence of turpentine as a solvent for caoutchouc, 204.
- Bouisson, M., on artificial marble, 405.
- Boussingault, M., on the development of mineral substances in the bones of pigs, 392.
- Bowman, J. E., on tribasic boracic æther, 287.
- Brande, Prof., on the electro-chemical protection of metals, 84.
- Breane, composition of, 151.
- British Association, proceedings of the, 406.
- Brockedon, W., on a method of forming the dust of graphite into a solid mass, 82.
- Brockelsby, Prof. J., on iridescent silver, 57.
- Bromine, estimation of, in mineral waters, 103.
- Bromo-boracic acid, composition of, 95.
- Bronzes, on some, 366.
- Brooks, T., on a series of double salts of the protoxide and peroxide of mercury, 35.
- Brunner, Prof. C., on the determination of carbonic acid in saline compounds, 366; on the manufacture of artificial ultramarine, 401.
- Buchner, W., on the presence of sulphuret of arsenic in shell-lac, 469.
- Bussy, A., on the employment of magnesia in the treatment of poisoning by arsenious acid, 293.
- Calcium, preparation of the sulphuret of, 304.
- Calculi, biliary, presence of copper in, 53.
- Calvert, Mr., on some new compounds of lead, 155.
- Cantharidine, analysis of, 44.
- Caoutchouc, essence of turpentine a solvent for, 204; on the formation of, 476.
- Capric acid, 375.
- Caprylic acid, 375.
- Carbonic acid, new method of estimating, 366.
- Carthamine, observations on, 378.
- Cartilage, amount of sulphur in, 363.
- Casaseca, M., on the estimation of copper, 302.
- Caseine, production of valerianic acid and a new substance from, 89; amount of sulphur in, 363.
- Cassebaum, M., on the preparation of the lactate of the protoxide of iron, 122.
- Cereus senilis*, on the occurrence of oxalate of lime in, 493.
- Cetraria Islandica*, examination of, 29, 54.
- Cetraric acid and salts, 32.
- Chalk, the copper sheathing of vessels preserved by, 183.
- Chancel, G., on the products resulting from the destructive distillation of the valerianate of barytes, 133.
- Chapman, E. J., on a new method of distinguishing baryta from strontia by the blowpipe, 299.

- Charcoal, improved preparation of, 436.
- Chelidonic acid and salts, examination of, 309, 336.
- Chemical Society, proceedings of the, 22, 125, 145, 167, 205, 227, 267, 285, 495.
- Chevallier, M., on the presence of lead, copper and arsenic in certain kinds of paper, and the processes necessary to discover such impurities, 361.
- Chloric acid, preparation of, 121.
- Chloride of silver, reduction of, 40.
- Chlorine, on the atomic weight of, 38, 169; new process for obtaining pure, 261.
- Chloro-acetic acid, preparation of, 73.
- Chlorocyanilide, observations on, 213.
- Cholacrole, 273.
- Cholesteric acid, 276, 366.
- Cholesterine, action of nitric acid on, 277.
- Cholic acid, action of nitric acid on, 365.
- Choloidanic acid, 275.
- Choloidic acid, action of nitric acid on, 269.
- Christison, Dr., on magnesia as an antidote to arsenic, 316.
- Chromic acid, advantageous method of preparing, 139; behaviour of, towards sulphuric acid, 140; reduction of, by ammonia, vapour of alcohol, &c., 152.
- Chromium, atomic weight of, 154; on the chromate of the oxide of, 317.
- Chrysolepic acid, on the salts of, 234.]
- Cinnamic acid and cinnamene, researches on, 90.
- Claus, Dr. C., on the chemical properties of ruthenium and some of its compounds, 437.
- Clémandot, M., on the production of artificial aventurine, 141.
- Cliff, J., on the manufacture of alum and aluminous compounds, 168.
- Cobalt, separation of, from phosphoric acid, 158; from manganese, 159.
- and zinc, on some double phosphates of, 156.
- Cobalt ore from Western India, analysis of a, 23.
- Cochineal, observations on, 46; new substance from, 168.
- Colours, preparation of some, 307.
- Coppering by galvanism, observations on, 45.
- Copper in biliary calculi, 53; improved method of precipitating, 128; new methods of estimating, 115, 300, 302; detection of minute quantities in organic fluids, 220; subnitrate of, 314; sulphocyanide of, decomposition of the, by sulphuretted hydrogen, 293.
- Copper ores, analysis of some Australian, 463.
- Cottureau, M., on chloride of platinum and starch as tests for iodine, 105; on a new method of estimating tin when this metal is alloyed with copper, 348.
- Coumarine, researches on, 267.
- Couturier, Messrs., on a method of extracting the iodine and bromine contained in the salts and mother-liquor of kelp-soda, 244.
- Crasso, G., analyses of the ashes of the vine, 233.
- Cruciferous plants, on the volatile oils of several, 252.
- Crystalline, amount of sulphur in, 363.
- Crystallography, observations on, 145.
- Cupola for melting iron, on an improved, 80.
- Cyanide of potassium, behaviour of various metals towards a solution of, 478.
- Cyanides of potassium and sodium, improvements in the manufacture of, 411.
- Cyanogen, analysis of the compounds of, 144.
- and iron, on the blue compounds of, 167.
- Cystine, on the relations between bile and, 471.
- Daguerreotypes, preparation of the gold solution for fixing, 49.
- Daubeny, Prof., on the rationale of certain practices employed in agriculture, 407.
- Delbos, M., on fluosilicanilide, 214.
- Deninger, C., analyses of the ashes of some plants, 231.
- Dessaignes, M., on hippuric acid, benzoic acid and sugar of gelatine, 14.
- Diesel, Dr., on the preparation of benzoic acid, 202; observations on myrrh, and on a method of distinguishing it from bdellium, 225.
- Diffuane, on the preparation and composition of, 98.
- Digestion and assimilation of amylaceous and saccharine substances, observations on, 196.
- Dilutric acid, formation and composition of, 111.
- Domonte, F., on a series of double phosphates of zinc and cobalt, 156; on a new method of estimating lead, 297.
- Dragonic acid, analysis of, 422.
- Dulk, F. P., on the testing of sodas, 20.
- Dumas, M., researches on the blood, 289.
- Dumasine, observations on, 362.
- Dumesnil, M., on the preparation of valerianate of zinc, 200.
- Dunlop, A., on the manufacture of ale, porter, &c., 288.
- Durocher, J., on the solubility of alumina in solution of ammonia, 347.

- Dyeing, improvements in, 48, 68, 127; employment of Rochelle salt in, 125.
- Dye-woods, new apparatus for extracting the colouring matter from, 122.
- Earthenware, improvements in producing patterns upon, 86.
- Eden, T. J., on apparatus used in the concentration of sulphuric acid, 328.
- Elaidic acid, 373; action of oxygen upon, 375.
- Elder tree, examination of the bark of the, 194.
- Electrical endosmose, observations on, 22.
- Electro-gilding, observations on, 326.
- — — and silvering, method of ascertaining the quantity of gold and silver consumed in, 143.
- Electrolysis, on the theory of, 125.
- Elsner, Dr. L., on the separation of gold and platinum from tin and arsenic, 39; on coppering by galvanism without the employment of cyanide of potassium, 45; on the preparation of purified solution of shell-lac, 82; on the quantitative separation of antimony from tin, 105; on the preparation of green copper colours free from arsenic, 307; on the behaviour of various metals towards an aqueous solution of cyanide of potassium, 478.
- Engelmann, C., analysis of the ash of *Secale cornutum*, 230.
- Epsom salts, improvements in the manufacture of, 187.
- Equivalents of simple bodies, notices respecting, 16, 38, 63, 154, 169.
- Erdmann, Prof., on the analysis of the ashes of plants, 230; on the non-existence of oxygen in picrotoxine, 394; on the analysis of nitrogenous substances, 395.
- Eudiometry, improvements in, 23, 287.
- Evre, St., on the citrate of the oxide of methyle, 192.
- Faber, A., on cochineal, 46.
- Fairy-rings, on the origin of, 384.
- Ferrocyanide of potassium, observations on, 38.
- Fibrine, amount of sulphur in, 363; on the composition of, 468.
- Filhol, M., on a method of detecting very minute quantities of copper in organic fluids, 220.
- Fischer, N. W., on some properties of selenium, 249.
- Flour, preparation of various kinds of, 67.
- Fluoric and phosphoric acids, separation of, from boracic acid, 186.
- Fluoride of calcium, solubility of, in water, 183.
- Fluosilicanilide, observations on, 214.
- Fly-powder, poisoning by, 356.
- Forchhammer, Prof., analytical researches on sea-water, 408.
- Fordos, M., on the action of perchloride of gold upon the hyposulphite of soda, 49; on the action of sulphur on potash and soda and their carbonates, 389.
- Formic acid, new process for obtaining, 320.
- Fownes, Dr., on the presence of phosphoric acid in felspar, 495.
- Frederking, M., on the preparation of valerianate of zinc, 200.
- Fremy, M., on the production of artificial aventurine, 141.
- Fresenius, R., on the solubility of some precipitates which occur in quantitative analysis, 479.
- Fritzsche, J., on a method of decomposing osmium-iridium, 319.
- Frogs, on the respiration of, 342.
- Fuci*, analyses of the ashes of some species of, 229.
- Funnel for filtering hot solutions, description of a, 364.
- Gallic acid, new method of preparing, 285.
- Galloway, Mr., analysis of the water from the King's Well, Bath, 496.
- Gaultier de Claubry, M., on the estimation of tin by volume, 455.
- Gay-Lussac, M., on the determination of silver, 282; on Leplay's theory of reduction, 346.
- Gelatine, on the products resulting from the oxidation of, by chromic acid, 10.
- Gelis, M., on the action of perchloride of gold upon the hyposulphite of soda, 49; on the action of sulphur on potash and soda and their carbonates, 389.
- Gerhardt, C., on bees-wax, 12; on the atomic weight of chlorine, 38; on the subnitrate of copper, 314.
- German silver, how to colour blue, 464.
- Gladstone, Mr., analysis of sand from St. Michael's Bay, Normandy, 496.
- Glasses, Bohemian, on the composition of some, 202.
- Gluten, amount of sulphur in, 363.
- Glycerine, conversion of, into metacetic acid, 292.
- Glycyrrhizine, observations on, 48 s of Gödechen's, J., analyses of the ashes some species of *Fuci*, 229.
- Gold, action of the perchloride of, upon the hyposulphate of soda, 49; on some new double salts of the protoxide of, 452; separation of, from tin and arsenic, 39; on the precipitation of, in the metallic state, 326.

- Goniometer, description of a new, 145.
- Goose-fat, examination of, 357, 372.
- Gorup-Besanez, Dr., on the presence of copper in bile, 291, 383.
- Gottlieb, Dr. J., examination of goose-fat and oleic acid, 357, 372.
- Goupil, E., on the nature of the acids contained in tobacco, 318.
- Grager, Dr. A., on the amount of ammonia contained in the atmosphere, 34.
- Graham, Prof., on a new eudiometric process, 23; on the proportion of water in the magnesian sulphates and double sulphates, 173; on the supply of iodine from the kelp of Guernsey, 495.
- Graphite, method of forming the dust of, into a solid mass, 82.
- Greenwood, Mr., on the manufacture of certain agents used in dyeing cotton, woollen, &c., 127.
- Gregory, Dr. W., on the preparation of alloxan, 23.
- Gregson, J. B., on the manufacture of Epsom salts and carbonate of lime, 187.
- Griffin, J., on the constitution of aqueous solutions of acids and alkalies, 227.
- Griffith, Dr. J. W., on the estimation of albumen in animal fluids, 283.
- Gris, M., on the action of soluble proto-salts of iron on vegetation, 200.
- Grove, Prof. W. R., on the decomposition of water into its constituent gases by heat, 406.
- Guaiacum wood, easy method of ascertaining the genuineness of, 80.
- Guaiacum resin, employment of, as a test, 368; process for detecting, 483.
- Guano, preparation of uric acid from, 482.
- Gum, preparation of artificial, 68.
- Gun-cotton, on the preparation and properties of, 430; on the chemical composition of, 496.
- Gutta Percha, observations on, 92.
- Gwynne, Mr., on the manufacture of soap, 207.
- Gypsum, solubility of, in water, 173.
- Hail, presence of hydrosulphuret of ammonia in, 150.
- Hece, Rees, on several new series of double oxalates, 72.
- Heine, M., on the quantitative estimation of bromine in mineral waters, 103.
- Heintz, W., on the quantitative determination of urea, potash and ammonia in urine, and on the composition of nitrate of urea, 17, 427; analysis of the milk of the cow-tree, 261; on dumazine, 362.
- Heller, Dr., on the detection of pus in blood and other fluids, 427.
- Hempel, C. W., on the products of oxidation of the essential oil of fennel, 421.
- Henry, M., on the preparation of valerianate of zinc, 200.
- Heraopath, T. J., on the oxidation of a lead-pipe, 419; on native sulphate of alumina, 422.
- Herberger, M., on the adulteration of iodine, 47; on the absorption of arsenic by plants, 493.
- Hermann, M., on the new metal ilmenium, 449.
- Himly, C., on two new series of double salts containing protoxide of gold, 452.
- Hippuric acid, on the constitution of, 11; decomposition of, into benzoic acid and sugar of gelatine, 14; preparation of, 461.
- Hoffmann, L., analyses of the ashes of some plants, 234.
- Hofmann, Prof., researches on aniline, 22; on the amount of carbonic acid, alcohol and extract of malt in Burton ale and pale ale, 78; on nitraniline, 167.
- Hopff, L., on the preparation and properties of angelic acid, 223.
- Horn, on a substitute for, 435.
- How, H., analysis of a Peruvian alloy, 495.
- Hruschauer, Dr. F., analyses of the ashes of Indian corn, 230.
- Hullmandel, C. J., on producing patterns upon earthenware and porcelain, 86.
- Huraut, M., on the preparation of the valerianate of zinc, 302.
- Hydrocyanic acid, on the preparation of pure, 399.
- Hydrosulphocyanic æther, preparation of, 222.
- Hydrylic acid, on the preparation and composition of, 100.
- Hypo-iodous acid, on the formation of, 318.
- Hypophosphites, on the constitution of the, 135.
- Hyponitric acid, action of, on chlorine and bromine, 205.
- Hyposulphite of soda, preparation of, 325.
- Icica resin, examination of, 151.
- Ilmenium, on the properties of, 449.
- Indian drugs, notices respecting some, 161.
- Inuline, composition of, 174.
- Iodide of potassium, mode of ascertaining the purity of, 457.
- Iodine, adulteration of, 47; tests for, 105; on the supply of, from the kelp of Guernsey, 495.
- Iron, improved cupola for melting, 80; incandescence of, in the vapour of alco-

- hol, 153, 315; action of the protosalts of, on vegetation, 200; new method of estimating, 216; separation of, from lime, 73; lactate of, preparation of the, 121, 122; on the products of decomposition of the protoxalate of, 470; how to prevent from rusting, 495.
- Iron and cyanogen, on the blue compounds of, 167.
- and steel, on the amalgamation of, 405.
- Isinglass, amount of sulphur in, 363.
- Jacquelain, M., on a quick method of determining copper, 300.
- Jalap resin, preparation of, 400.
- James, H., analyses of the ashes of some plants, 233.
- Jamieson, A. J., on the decomposition of the sulphocyanide of lead and copper by sulphuretted hydrogen, 293.
- Jonas, M., on the preparation of the ferrocyanide of zinc, 388; on the artificial production of caoutchouc, 476.
- Jones, Dr. H. B., on the variations in the alkaline and earthy phosphates in disease, 226.
- Jones, R. L., on the preparation of charcoal, 436.
- Joule, J. R., on atomic volume and specific gravity of elementary bodies, their oxides, &c., 126; on the maximum density of water, 228.
- Kelp soda, method of extracting the iodine and bromine contained in the salts and mother-liquor of, 244.
- Kemp, Dr. G., on a method of separating the body produced by the joint action of sulphuric acid and sugar on ox-bile, 278; on the constitution of the human bile, 294; on the theory of proteine, 369, 477; on the determination of nitrogen in organic bodies, 454; on the quantity of sulphur in bile, and on the relations between it, taurine, cystine, and lithofellic acid, 471.
- Kipp, T., on the employment of the sulphocyanide of potassium as a test for ascertaining the purity of nitric acid, 346.
- Knop, W., on *Cetraria Islandica*, 29, 54.
- Kobell, Dr. von, on the separation of phosphoric acid, 158; on the detection of sulphur, and on a method of distinguishing sulphurets from sulphates, 160; on the separation of boracic acid from phosphoric and fluoric acids, 186.
- Köchlin, H., analyses of the ashes of some plants, 234.
- Kœne, Prof., on the formation of hypoiodous acid, and the reactions which occur in the metamorphoses of this acid, 318.
- Kolbe, Dr., on the formation of nitric acid in eudiometric analyses, 287.
- Kopp, E., on cinnamic acid and cinnamene, 90.
- Kramer, H., on the inner bark of the elder tree, 194.
- Krocker, Dr., examination of some kinds of marl, 385; on the determination of the amount of starch in the various kinds of vegetable food, 453.
- Lactate of iron, preparation of, 121, 122.
- Lactic acid, on the formation of, 492.
- Lade, Dr. T., on glycyrrhizine, 488.
- Lados, M., on the presence of arsenic in soot, 114.
- Laming, J., on the manufacture of the cyanides and ferrocyanides of potassium and sodium, 411.
- Larocque, M., on the adulteration of the valerianate of zinc, 302.
- Laskowski, N., on the theory of proteine, 329.
- Lassaigne, M., on a method of distinguishing arsenic from antimony, 106.
- Laurent, Aug., on chlorocyanilide, 213; on fluosilicanilide, 214; on the composition of sugar of gelatine, 492.
- Laurus Sassafras*, examination of the bark of, 215.
- Lavini, M., on several species of *Meloe*, 44.
- Lead, new salts of, 77, 155; new method of estimating, 297; separation of, from bismuth, 221; on the adulteration of the carbonate of, 493.
- , sulphocyanide of, on the decomposition of the, by sulphuretted hydrogen, 293.
- Lead-pipe, curious oxidation of a, 419.
- Leblanc, J., on the property of litharge in a state of fusion of absorbing oxygen, 62.
- Leeson, Dr., on crystallography, 145.
- Leifchild, J., on the manufacture of blue to be used as a substitute for stone-blue, 128.
- Legumine, on the amount of sulphur in, 363; analysis of, 364.
- Lepage, M., on a new method of preparing lactate of iron, 121.
- Lepidium rudemale*, on the volatile oil of, 253.
- Lerch, J. U., on chelidonic acid and its salts, 309, 336.
- Letellier, F., on the influence of temperature upon the respiration of warm-blooded animals, 64.
- Letheby, Dr. H., on the detection of arsenic in organic mixtures, 137; on

- the action of oxalic acid upon the blood and dead tissues, 408; on the difference in the physiological actions of the yellow and red prussiates, 410.
- Leuchtenberg, Duke of, on a method of ascertaining the quantity of gold and silver consumed in electro-gilding and silvering, 143.
- Leucoturic acid, preparation and composition of, 97.
- Levol, A., on a simple method of reducing chloride of silver, 40; on the quantitative determination of arsenic in alloys and minerals, 159; on the estimation of silver by the moist process, 184; on the bibasic arseniate of ammonia and magnesia, 296.
- Lichetearic acid and salts, examination of, 54.
- Liebig, Prof. J., on the production of valerianic acid and a new substance from caseine, 89; on the absence of alkaline carbonates in the blood, 94; on bin-oxide of proteine, 101.
- Lime, separation of, from iron, 73.
- Litharge, absorption of oxygen by, 62.
- Lithofellic acid, on the relations between bile and, 471.
- Loewig, M., on the preparation of hydro-sulphocyanic æther, 222.
- Louyet, Prof., on a new mercurial trough, 221; on the adulteration of white lead, 493.
- Lucas, M., on the occurrence of oxalate of lime in *Cereus senilis*, 493.
- Lucifer-matches, manufacture of, 405.
- Lüdersdorf, Dr., on the nature of yeast, 281.
- Ludwig, Dr. C., on the extractive matters of the blood, 73.
- MacLagan, Dr. D., on gutta serena, 92; on an impurity occurring in commercial *Aqua ammoniac*, 283.
- Madder, analysis of the ashes of the, 232.
- Magnesia an antidote for arsenic, 293, 316.
- and ammonia, on the bibasic arseniate of, 296.
- Magnesian sulphates, on the proportion of water in the, 173.
- Malaguti, M., on the preparation of chloro-acetic acid, 73; on the solubility of alumina in solution of ammonia, 347.
- Manganese, separation of, from cobalt, 159; on the red colour of the proto-salts of, 396.
- Mannite, preparation of, 387.
- Manures, artificial, 206.
- Marble, manufacture of artificial, 405.
- Marchand, Prof. R. F., on the products resulting from the oxidation of gelatine by chromic acid, 10; on the presence of carbonates in the blood, 209; on the respiration of frogs, 342; on the non-existence of nitrogen in picrotoxine, with observations on the analysis of nitrogenous substances, 394; on the colour of the blood, 417.
- Mareska, M., on the presence of arsenic in soot, 114.
- Marguerite, H., on a new method for the quantitative determination of iron, 216.
- Marignac, Prof., on the atomic weight of chlorine, 169.
- Marl, examination of some kinds of, 385.
- Maugham, W., on the manufacture of ale, porter, and other fermented liquors, 288.
- Maumené, E., on the reciprocal action of metals and concentrated sulphuric acid, 448.
- May, A., analyses of the ashes of madder, 232.
- Meier, Leo., chemical investigation of the red poppy, 192.
- Meloe, examination of some species of, 44.
- Melsens, M., on the transparency of quicksilver, 57.
- Mercer, Mr., on the manufacture of certain chemical agents used in dyeing, 127.
- Mercurial trough, description of a new, 221.
- Mercury, on some double salts of the per- and protoxide of, 35; estimation of, 119; on the changes experienced by, in sealed glass vessels, 410; on the purification of, 482.
- Metacetic acid, preparation of, from glycerine, 292.
- Metals, on the electro-chemical protection of, 84; improved methods of separating, 23, 65; precipitation of some, by sulphuretted hydrogen, 221; behaviour of various, towards a solution of cyanide of potassium, 478.
- and sulphuric acid, on the reciprocal action of, 448.
- Methyle, on the citrate of the oxide of, 192.
- Meyer, M., on the volatile acids in *Angelica officinalis*, 129.
- Mialhe, M., on the employment of the oxalate of alumina in the manufacture of cane and beet-root sugar, 142; on the digestion and assimilation of amy-laceous and saccharine substances, 196.
- Middleton, Prof., analysis of a cobalt ore found in India, 23.
- Milk, on the influence of different kinds of food on the production of, 258.

- Milk of the cow-tree, analysis of, 261.
 Milk-sugar, presence of, in incubated eggs, 280.
 Millon, E., on the quantitative determination of mercury, 119; on the decomposition of water by metals, 132.
 Mineral waters, estimation of bromine in, 103.
 Mitscherlich, Prof., on the analysis of the ashes of yeast, 69.
 Monro, von L., on the volatile acids in *Viburnum Opulus*, 9.
 Montriers, J. H., on a combination of prussian blue and ammonia, 157.
 Moss, T. F., on the cleaning of the wire-cylinder of the safety-lamp, 246.
 Muck, Mr., analysis of the water of the King's Well, Bath, 496.
 Mueller, F., on a method of preparing gallic acid, 285.
 Mulder, G. J., on vegetable mucilage, 313.
 Murdoch, J., on dyeing, 68.
 Musk-pods, method for detecting spurious, 79.
 Muspratt, Dr., on nitraniline, 167.
 Myrrh, observations on, 225.
 Napier, J., on an improved method of separating metals, 65; on electrical endosmose, 22; on the unequal decomposition of electrolytes and the theory of electrolysis, 125.
 Neligan, Dr. J. M., on a new method of detecting spurious musk-pods, 79.
 Nesbit, J. C., on the employment of phosphoric acid for detecting alumina, 127.
 Newton, W., on improvements in dyeing cotton, 48.
 Nicholson, E., on the compounds of phosphoric acid with aniline, 286.
 Nicotianine, composition of, 76.
 Nicotic acid, composition of, 76.
 Niobic acid, on some properties of, 351.
 Nitraniline, 167.
 Nitric acid, method of ascertaining the purity of, 346.
 Nitric oxide, on the sulphite of, 335.
 Nitrocholic acid, 273.
 Nitrogen, equivalent of, 63; estimation of, 454, 395.
 Nitro-hydurilic acid, on the preparation and composition of, 109.
 Nitrophenic acid, on the salts of, 237.
 Nitrous oxide, influence of, on vegetation, 371.
 Oenanthic acid, on the formation of, 13.
 Oersted, Prof., on the changes which mercury sometimes suffers in glass vessels hermetically sealed, 410.
 Oil of fennel, on the products of the oxidation of, 421.
 Oil of *Monarda*, on the composition of, 474.
 Oil of mustard, observations on, 252.
 Oleic acid, on the products resulting from the oxidation of, with nitric acid, 285; examination of, 357; action of oxygen upon, 372.
 Oost, van A. J., on materials used for fertilizing land, 206.
 Osann, G., on the employment of guaiacum-resin as a test, 368; on platinum in the oxidized state, 447.
 Osmium-iridium, advantageous method of decomposing, 319.
 Otto, Prof., on the preparation of gun-cotton, 431.
 Oxalates, on several new double, 72.
 Oxalic acid, action of, upon the blood and dead tissues of the animal body, 408.
 Palmitic acid, researches on, 286.
Papaveraceæ, examination of some, 197.
 Papaveric acid, 193.
 Paper, on the presence of lead, copper and arsenic in, with methods of detecting, 361.
 Payen, M., on the presence of lead, copper and arsenic in paper, 361.
 Pearlashes, new method of estimating the value of, 163.
 Peligot, E., on the composition of some glasses manufactured in Bohemia, 202; on a new process for the estimation of sugar, 305; on the composition of the salts of antimony, 444.
 Pelletier, M., on the presence of hydro-sulphuret of ammonia in hail, 150.
 Pelouze and its compounds, 349.
 Pelouze, J., on the equivalents of some simple bodies, 63; on a new method of estimating copper, 115.
 Pentathionic acid, properties of, 465.
 Percy, Dr., on a gas furnace for organic analysis, 408.
 Personne, J., on the preparation of alcoholic tinctures, 41.
 Pesier, Ed., on a new method of estimating the value of pearlashes, 163.
 Pettenkofer, Max., on the presence of sulphocyanogen in human saliva, 189.
 Phosphoric acid, on the separation of, 158; separation of, from boric acid, 186; preparation of pure, 201; on the presence of, in felspar, 495.
 Phosphorus, atomic weight of, 64; influence exerted by electricity, platinum and silver on the shining of, 148.
 Picric acid, on the salts of, 238.
 Picrotoxine, observations on, 394.
 Pierre, J. L., on some double salts of the magnesian group, 113.

- Pinel, J. F., on the mode of treating farinaceous substances, 67.
- Plantamour, M., on a water-bath funnel for filtering hot solutions, 364.
- Plants, analyses of the ashes of, 229; experiments on the absorption of arsenic by, 493.
- Platinum, separation of, from gold, tin and arsenic, 39; on a peculiar oxidized state of, 447.
- Playfair, Dr. L., on atomic volume and specific gravity of elementary bodies, their oxides, &c., 126; on the maximum density of water, 228; on palmitic acid, 286.
- Pless, F., on the volatile oils of several cruciferous plants, 252.
- Poggiale, M., on some new double haloid salts, 76; on bromo-boracic acid and bromo-borate of ammonia, 95.
- Poppy, chemical examination of the flowers of the, 192.
- Porcelain, improvements in producing patterns upon, 86.
- Porphyroxine, observations on, 198.
- Porrett, R., on the chemical composition of gun-cotton, 496.
- Porter, improvements in the manufacture of, 288.
- Potassium, atomic weight of, 63; preparation of the ferridcyanide of, 401.
- Potato-flour, mode of preparing, 107.
- Precipitated chalk, improvements in the manufacture of, 187.
- Precipitates, on the solubility of some, 479.
- Prize questions, notice of, 423.
- Proteine, on the binoxide of, 74, 101; on the theory of, 329, 369; on the chloride of, 477.
- Prussian blue and ammonia, on a combination of, 157.
- Prussiates, on the difference in the physiological actions of the yellow and red, 410; improvements in the manufacture of the, 411.
- Prussic acid, new test for, 220; preparation of pure, 399.
- Pus, detection of, in blood and other fluids, 427.
- Pyrophorus from tartar-emetic, 35.
- Quicksilver, transparency of, 57.
- Radix sanguinaria*, examination of, 197.
- Rammelsberg, Dr. C., on the atomic weight of uranium, 16; on the salts of sulphurous acid, 254; on the chromate of the oxide of chromium, 317; on the products of decomposition of the protoxalate of iron, 470.
- Raphanus sativus*, on the volatile oil of, 254.
- Redtenbacher, Prof. J., on the composition of taurine, 238; on the action of nitric acid upon choloidic acid and cholesterine, 269; on the volatile fat acids arising from the oxidation of oleic acid by means of nitric acid, 285; on the conversion of glycerine into metacetic acid, 292.
- Reduction, on Leplay's theory of, 346.
- Reh , J. H., on the manufacture of starch and farinaceous food, 247.
- Reinsch, Dr., on the incandescence of iron, copper and other metals, 153, 315; on a new acid in the root of *Robinia*, 199; on the bark of the root of *Laurus Sassafras*, 215; on the preparation and properties of angelic acid, 223; on assaf etida, 444; on a method of cleansing retorts and glass vessels, 494.
- Respiration, influence of temperature upon, 64; on the theory of, 342.
- Retorts, method of cleaning, 494.
- Rheadic acid, examination of, 193.
- Rieckher, Dr. T., on the salts of picric, nitrophenisic and chrysolepic acids, 234.
- Riegel, Dr., on some *Papaveraceae*, 197; on the preparation of sulphuret of calcium, 304; of ferridcyanide of potassium, 401; of caustic baryta, 461; of the golden sulphuret of antimony, 462.
- Robinia*, examination of the root of, 199.
- Robinic acid, 199.
- Rocella tinctoria*, on the substances contained in, 206.
- Rochon, M., on a substitute for horn, 435.
- Rogers, Profs., on a new process for obtaining pure chlorine gas, 261; on a new process for obtaining formic acid, and on the preparation of aldehyde and acetic acid, 320.
- Ronalds, E., on the analysis of some Australian copper ores, 463.
- Rose, Prof. H., on the new metal pelopium, 349; on the new metal ilmennium, 451; on the peculiar phenomenon observed in the solidification of silver, 485.
- Royal Institution, proceedings of the, 84.
- Royal Society, proceedings of the, 144, 226.
- R lling, Dr. E., analysis of the ashes of some plants, 233; on the determination of the sulphur in the nitrogenous constituents of vegetable and animal bodies, 362.
- Runge, Dr. F. F., on the ferrocyanide of potassium, 38.
- Ruspini, G., on an easy and advantageous method of preparing mannite, 387.

- Ruthenium and its compounds, on the properties of, 437.
- Safety-lamp, method of cleansing the, 246.
- Safflower, on the red and yellow pigments of, 376.
- Saliva, human, on the presence of sulphocyanogen in, 189, 240.
- Salts, on some new double haloid, 76; new double, of the magnesian group, 113.
- Sanguinarine, examination of, 197.
- Sassafrid, 215.
- Schaffaeutl, Dr. C., on the manufacture of steel, 262.
- Scherer, Prof., on the extractives of the urine, 177.
- Schlieper, A., on alloxan, alloxanic acid, and some new products of decomposition of uric acid, 1, 96, 110; on the determination of the sulphur in the nitrogenous constituents of vegetable and animal bodies, 362; on the action of nitric acid upon cholic acid, 365; on the red and yellow pigments of safflower, 376; on the cyanurate of the oxide of amyle, 420.
- Schlossberger, Prof., on the composition of fibrine, 468.
- Schlumberger, L., on a new apparatus for extracting the colouring matter from dye-woods, 122.
- Schmidt, C., analyses of the ashes of wheat, 230.
- Schnedermann, Dr., on *Cetraria Islandica*, 29, 54.
- Schobben, Dr. de, on poisoning with fly-powder, 356.
- Schönbein, Dr. C. F., on the influence exerted by electricity, platinum and silver on the shining of phosphorus, 148; on spontaneous nitrification, 145; on the action of hyponitric acid upon aqueous solutions of bromine and chlorine, 205.
- Schwacke, J. H., on a method of ascertaining the genuineness of guaiacum wood, 80.
- Scribe, F., on Icaica resin, 151.
- Sea-water, comparative analyses of, 408.
- Sebacic acid, 375.
- Selenium, on some properties of, 249.
- Shell-lac, preparation of a purified solution of, 82; on the presence of sulphuret of arsenic in, 469.
- Shiel, Dr. J., on the supposed property of the bile of converting sugar into fat, 242.
- Silicic acid, on the specific gravity of, 355.
- Silicium, atomic weight of, 64.
- Silver, notice respecting iridescent, 57; estimation of, by the moist process when containing mercury, 184, 282; on the peculiar phenomenon observed in the solidification of, 485.
- Smedt, M. de, on the employment of chloride of soda for detecting the presence of guaiacum resin, 483.
- Smith, A., on the manufacture of soda ash, 308.
- Smith, J. L., on the freezing of water by the air-pump, 134.
- Smith, R., on the decomposition and analysis of the compounds of ammonia and cyanogen, 144.
- Snyder, S., on improvements in tanning, 108.
- Soap, improvements in the manufacture of, 207.
- Sobrero, M., examination of several species of *Meloe*, 44.
- Soda ash, improvements in the manufacture of, 308.
- Sodas, on the testing of, 20.
- Sodium, atomic weight of, 63.
- Soubeyran, E., on the preparation of jalap resin, 400.
- Souchay, A., analyses of the ashes of some plants, 231, 234.
- Stannates, on the manufacture of certain, 127.
- Starch, action of tannin upon, 65; improvements in the manufacture of, 247; estimation of, 453; from *Cetraria Islandica*, observations on, 56.
- Steel, on the manufacture of, 262.
- Strontia, method of distinguishing, from baryta by the blowpipe, 299.
- Strontium, atomic weight of, 64.
- Struvite, description of, 148.
- Sugar, improvements in the manufacture of, 142; action of, on tartaric acid, 149; new process for the estimation of, 305.
- Sugar of gelatine, researches on, 14; on the composition of, 492.
- Sulphates, method of distinguishing, from sulphurets, 160.
- Sulphocyanide of lead and copper, on the decomposition of, by sulphuretted hydrogen, 293.
- of potassium, employment of, as a test, 346.
- Sulphocyanogen in human saliva, 189, 240.
- Sulphur, simple method of detecting, 160; determination of the amount of, in the nitrogenous constituents of vegetable and animal bodies, 362, 370; action of, on potash and soda and their carbonates, 389; on a new acid of, 465.
- Sulphuric acid, improvements in the manufacture of, 328.

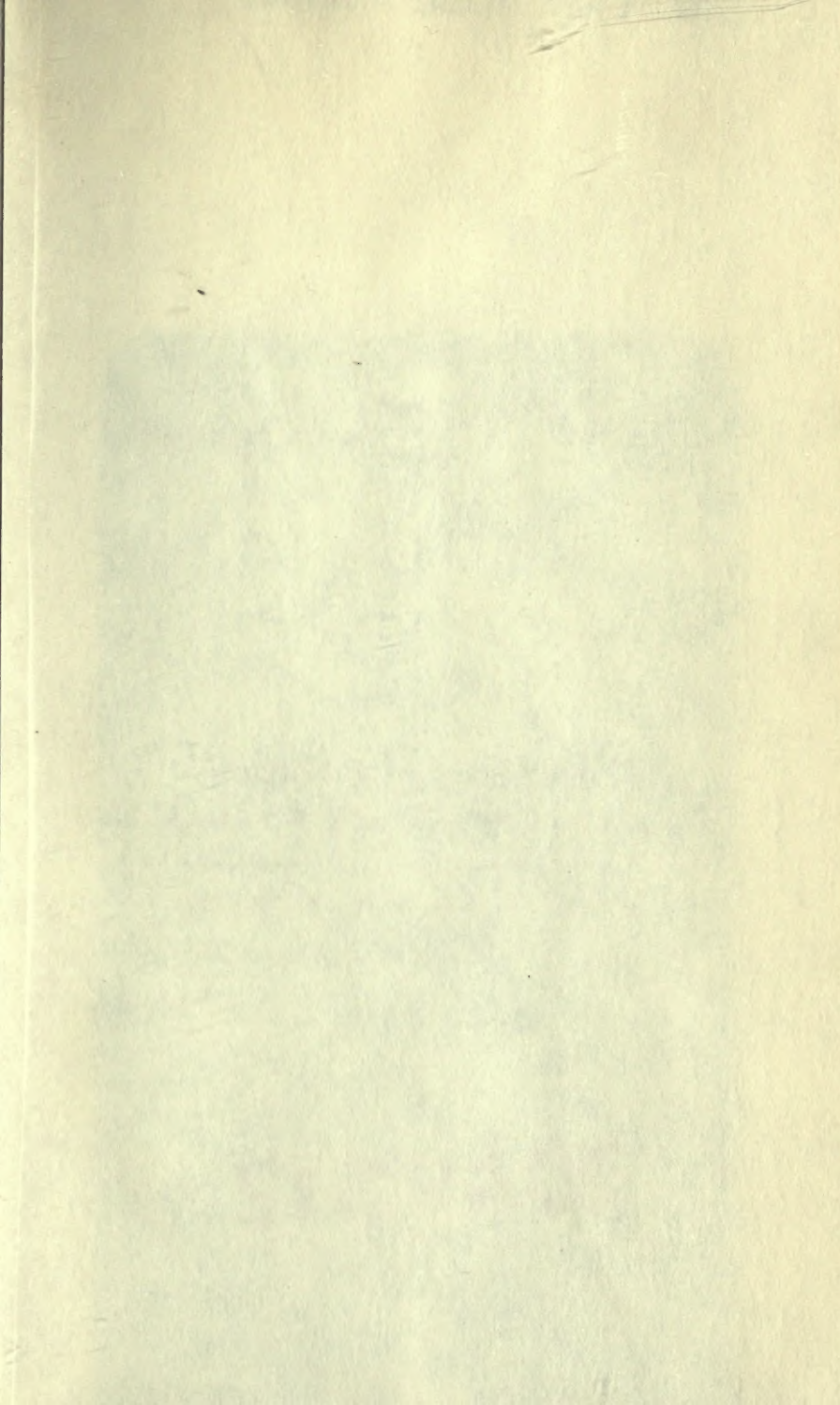
- Sulphuric acid and metals, on the reciprocal action of, 448.
- Sulphurous acid, on the salts of, 254; method of detecting, 424.
- Tannin, action of, upon starch, 65.
- Tanning, improvements in, 108.
- Tantallic acid, on some properties of, 351.
- Tartar-emetic, pyrophorus from, 35.
- Tartaric acid, action of sugar on, 149.
- Taurine, on the composition of, 238, 281; on the relations between bile and, 471.
- Taylor, J., on separating metals, 23.
- Taylor, T., on the preparation of gun-cotton, 431.
- Teschemacher, E. F., on the chemical composition of gun-cotton, 496.
- Thallochlor, on the composition of, 31.
- Thlaspi arvense*, on the volatile oil of, 252.
- Thompson, J., on the preparation and application of various farinaceous products, 107.
- Thomson, Dr. R. D., on the influence of different kinds of food on the production of milk and butter, 258.
- Tin, separation of, from platinum, gold and arsenic, 39; from antimony, 105; new methods of estimating, 348, 455; new double salts of, 76; on crystallized oxide of, 386; action of sulphurous acid on, 424.
- Tinctures, on the preparation of, 41.
- Tobacco, on some new substances from, 76, 318.
- Törner, J., on crystallized oxide of tin, 386.
- Turpentine-camphor, observations on, 364.
- Ulex, M. G. L., on struvite, 148; on the purification of mercury, 482.
- Ultramarine, on the manufacture of, 401.
- Umbellie acid, 421.
- Uranium, on the atomic weight of, 16; method of purifying the oxide of, 78.
- Urea, on the quantitative determination of, 17, 427; on the composition of the nitrate of, 18; combinations of, with salts, 59; remarks on the constitution of, 62.
- Urethane, on the formation of, 175.
- Uric acid, on some new products of decomposition of, 1; on the preparation of, 482.
- Urine, on the estimation of the urea, potash and ammonia in, 17, 427; on the extractives of the, 177; colouring matter of the, 179; contributions to the chemistry of the, 226.
- Valerianate of zinc, preparation of, 200, 302.
- Valerianate of barytes, on the products resulting from the destructive distillation of, 133.
- Valerianic acid, occurrence of, in *Viburnum Opulus*, 9; production of, from caseine, 89.
- Vegetable mucilage, observations on, 313.
- Vegetables, on a new method of determining the amount of starch in, 453.
- Vegetation, action of the soluble proto-salts of iron on, 200; influence of nitrous oxide on, 371.
- Verdeil, F., on the determination of the sulphur in the nitrogenous constituents of vegetable and animal bodies, 362; on crystallized bile, 486.
- Viburnum Opulus*, on the volatile acids of, 9.
- Vine, analyses of the ashes of the, 232.
- Vogel, M., on the action of sugar on tartaric acid, 149; on the precipitation of some metals with sulphuretted hydrogen, 221; on the influence of protoxide of nitrogen upon vegetation, 371.
- Völker, A., on the red colour of the protosalts of manganese, 396.
- Wackenroder, Prof., on the preparation of a pyrophorus from tartar-emetic, 35; on the action of protochloride of tin and of metallic tin upon sulphurous acid, 424; on a new acid of sulphur, 465; on the formation of lactic acid, 492.
- Waidele, M., on a mode of dividing plates of zinc, 396.
- Walther, Dr., on the determination of sulphur in the nitrogenous constituents of vegetable and animal bodies, 362.
- Warington, R., on the preservation of animal and vegetable substances, 484.
- Water, decomposition of, by metals, promoted by the presence of acids or salts, 133; freezing of, by the air-pump, 134; maximum density of, 228; decomposition of, by heat, 406.
- Waters, mineral, analyses of some, 496.
- Way, J. T., on the fairy rings of pastures, 384.
- Werther, Dr., on the combinations of urea with salts, 58.
- West, B., on stoppering the tops of bottles, 248.
- Wheat, analyses of the ashes of, 230.
- White lead, on the adulteration of, 493.
- Wiggers, M., on turpentine-camphor, 364.
- Wilson, Dr. G., on the solubility of fluoride of calcium in water, 183.
- Wilson, Messrs., on the manufacture of soap, 207.
- Winckler, F. L., on the preparation of pure phosphoric acid, 201; on the pre-

- sence of milk-sugar in incubated eggs, 280.
- Winder, W., on some Indian remedies, 161.
- Wöhler, Prof., on a method of purifying oxide of uranium from nickel, cobalt and zinc, 78; on the preparation of pure hydrocyanic acid, 399.
- Woskressensky, A., on the composition of inuline, 174.
- Wright, Dr. S., on the estimation of the sulphocyanogen in the saliva, 240.
- Wrightson, F., analyses of the ashes of some plants, 231.
- Wurz, A., on the constitution of the hypophosphites, 135; on the formation of urethane, 175.
- Xyloidine, on the preparation and properties of, 430.
- Yeast, analysis of the ashes of, 69; on the nature of, 281.
- Zeni, M., on preserving iron from rust, 495.
- Zenner, M., on the volatile acids in *Angelica officinalis*, 129.
- Zinc, new double salts of, 77, 113; preparation of the ferrocyanide of, 388; mode of dividing plates of, 396.
- and cobalt, on some double phosphates of, 156.

END OF VOLUME IV.

PRINTED BY RICHARD AND JOHN E. TAYLOR,
RED LION COURT, FLEET STREET.





P
Chem & Phys
C

Chemical gazette.

v. 4

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY

STORAGE

